Synthesis, Structures, and Crystalline Packing Features of [Co(tren)(amino acidato-*N*,*O*)]$X_2 \cdot nH_2O$ (X = ClO_4^-, I^-)

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Keywords: Cobalt / Tripodal ligands / N ligands / Amino acids

The crystal structures of several novel compounds, *trans*(*N*,*t*-*N*) isomers of [Co(tren)(DL-phenylalaninato)]$(ClO_4)_2$ (**1**), [Co(tren)(L-phenylalaninato)]$I_2 \cdot H_2O$ (**2**), [Co(tren)(L-prolinato)]$I_2 \cdot H_2O$ (**3**), [Co(tren)(L-tryptophanato)]$(ClO_4)_2 \cdot {}^1/_2H_2O$ (**4**), [Co(tren)(L-valinato)]$I_2 \cdot {}^1/_3H_2O$ (**5**), [Co(tren)(L-isoleucinato)]I_2 (**6**), and [Co(tren)(L-leucinato)]I_2 (**7**), have been determined. Their packing arrangements indicate that the complex cations in all of the compounds form helical strings running along their crystallographic axes, for both chiral and racemic amino acidato species. Intermolecular double and single hydrogen bonds are formed by the carbonyl oxygens and amino hydrogens of the tren ligand or of the amino acidato moiety, either directly or by the assistance of water molecules of hydration. In this fashion, [Co(tren)(amino acidato-*N*,*O*)]$^{2+}$ is strung together into helical arrays. In the racemic compounds, the complex cations of different strings have opposite chirality. Phenylalanine is racemized during the coordination process, under mild pH (7.5–8.0) and temperature (60 °C). This is quite unusual. Finally, 1D and 2D (COSY) ^{1}H NMR spectra were recorded, in which compound **4** shows interesting cross-peak correlations between the phenyl protons and amino protons.

Introduction

Recently, it was reported[1] that the monooxamide anion is hydrolyzed by dihalo-Co^{III} complexes containing various types of polyamine tetradentate ligands, such as $(en)_2$, 3,2,3-tet (1,5,8,12-tetraaminododecane), trien, or tren, to give their corresponding oxalato compounds. Thus, we decided to systematically investigate the mechanism of this hydrolytic process of amide and peptide cleavage catalyzed by *cis*-$[CoN_4Cl_2]^+$, in comparison with that of *cis*-$[CoN_4(H_2O)(OH)]^{2+}$ reported by Buckingham, et al.[2–9] Of particular interest are the chiral and stereochemical problems associated with this process.

Our first efforts were directed towards the synthesis and characterization of the structures of $[Co(N_4)(\text{amino acidato})]^{2+}$ (N_4 = trien and tren) complexes with different types of amino acids. This data could then be used to help identify the steric nature of the hydrolysis products, which is not available crystallographically. Here, we report the crystal structures, including packing features, of seven novel *trans*(*N*,*t*-*N*) isomers of [Co(tren)(DL-phenylalaninato)]$(ClO_4)_2$ (**1**), [Co(tren) (L-phenylalaninato)]$I_2 \cdot H_2O$ (**2**), [Co(tren)(L-prolinato)]$I_2 \cdot H_2O$ (**3**), [Co(tren)(L-tryptophanato)]$(ClO_4)_2 \cdot {}^1/_2H_2O$ (**4**), [Co(tren)(L-valinato)]$I_2 \cdot {}^1/_3H_2O$ (**5**), [Co(tren)(L-isoleucinato)]I_2 (**6**), [Co(tren)(L-leucinato)]I_2 (**7**), where *trans*(*N*,*t*-*N*) refers to one of the two possible geometric isomers in which the tertiary nitrogen atom of tren is in the position *trans* to the amide nitrogen of the amino acidato cation.[10]

The starting amino acids used for the preparation are all of the natural L form. The DL-phenylalaninato was obtained as a result of racemization during the synthesis in mild pH (7.5−8.0) and temperature (60 °C). Finally, of particular interest is the observation that chiral helical arrays are observed in all of the crystals examined, both in the optically active and the racemic forms of amino acidato complexes.

Results and Discussion

Racemization of Phenylalanine

The starting materials used in this study were all of the natural L form of the amino acids. Interestingly, we found that one of the amino acids, phenylalanine, racemized during the process of preparation under very mild conditions of pH (7.5−8.0) and temperature (60 °C); while no crystallographic evidence of racemization was observed for the other amino acids involved in this study. The mechanism of amino acid racemization reactions involves the removal of the α-hydrogen and the stabilization of the resulting planar carbanion. It has been reported that racemization of phenylalanine takes place in vitamin B_6-amino acid Schiff base copper complexes in mildly acidic solutions,[11] in which the activation of the αC−H group is due to the π-π intermolecular interaction which is claimed to be the reason

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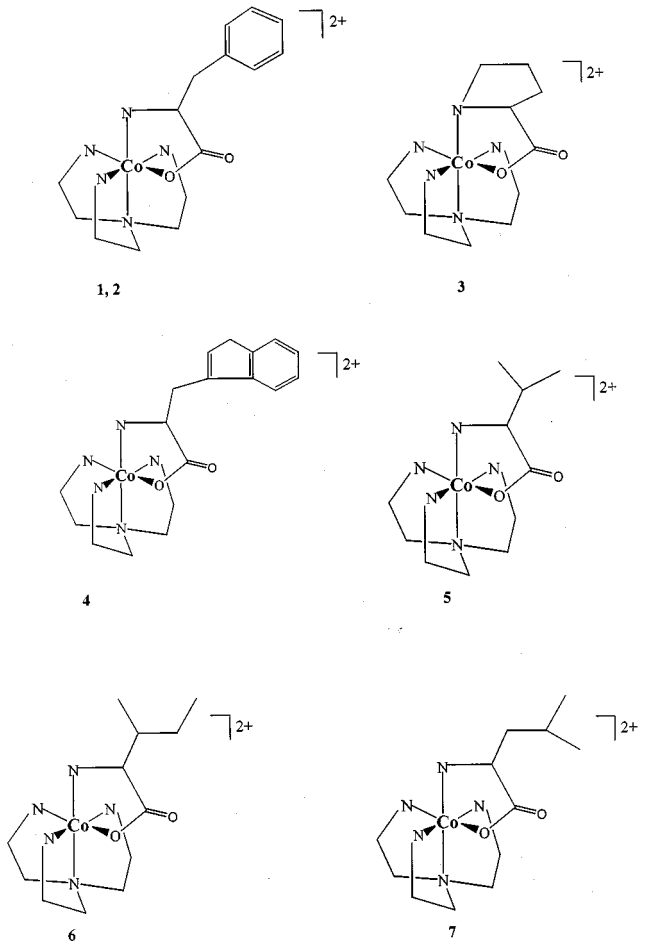

for the unusual racemization. Racemization of phenylalanine has also been observed in bis(2,2′-bipyridine) ruthenium(II) complexes in basic solution.[12] The asymmetric transformation of α-amino acids promoted by optically active Co^{III} complexes at pH 10−12 carbonate buffer has been examined by Yamaguchi.[13] However, the influence of substituents of the amino acid on the isomerization process was not elucidated, and further efforts are required to explain the unusual phenylalanine racemization observed in this study, for the following reasons: (1) It takes place under rather mild condition; (2) No crystallographic evidence of racemization is observed for other chelated amino acids, such as proline, tryptophan, valine, isoleucine, and leucine, under the same solution conditions.

Finally, we are aware that the fact that some of these complexes crystallize in enantiomorphic space groups does not necessarily mean that they are pure optically active compounds to begin with. It could be the result of conglomerate crystallization of the racemates.[14] Therefore, other experimental measurements, such as CD spectra, were required to exclude the possibility that other amino acids were racemized under the same conditions, and then proceeded to undergo conglomerate crystallization. Such a process has been documented in the case of Schiff base.[15]

Description of the Structures and Packing

Compounds **1** and **2**: With regard to the conformation of the coordination sphere, the most obvious difference between these two complexes is the orientation of the phenyl rings, as indicated in Figure 1 and Figure 2. The ^1H NMR spectra of these two compounds are identical implying that packing effects could be the driving force for this difference. In compound **1**, a single hydrogen bond between the carbonyl oxygen of one complex and the amino hydrogen of the amino acidato ligand from an adjacent complex leads to a head-to-tail linking of complexes of the same chirality to form cation strings running along the *c* axis. Looking down the *c* axis, one can see a column-like structure of the complexes, with the phenyl rings stacked on top of one another. The counter anions fill the gaps between the columns.

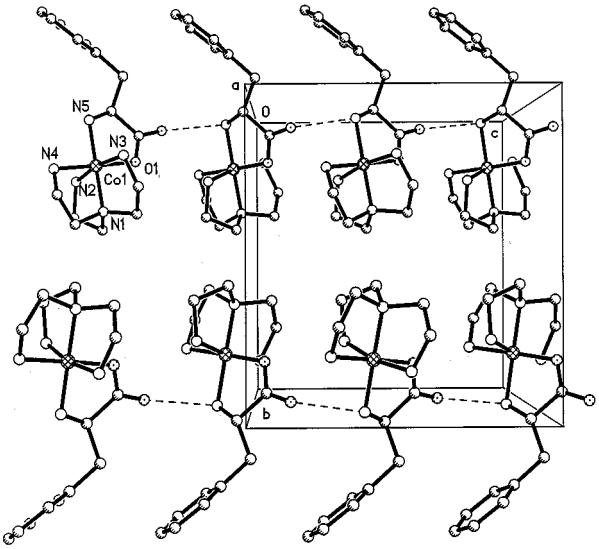

Figure 1. Spiral strings formed by the cations in the racemic compound **1**. The chirality of phenylanine shown is D. Cation strings run along *c* axis. When looking down along the *c* axis, phenyl rings and cations pack on top of each other, forming a column-like structure. Selected bond lengths: Co1−O1 1.903(3), Co1−N1 1.945(4), Co1−N2 1.955(4), Co1−N3 1.979(4), Co1−N4 1.954(4), Co1−N5 1.948(4) Å

The optically active form of compound **2** has a similar hydrogen-bonding motif, except that the chain runs along the *a* axis, and the phenyl rings are positioned around the chain axis.

Compounds **3**−**5**: Figure 3 shows that in compound **3** the cations are 'stitched' together in zigzag chains by an intermediary water molecule. In compound **4**, there are two independent molecules in the asymmetric unit. Figure 4 shows that the hydrogen-bonding motif is slightly different from that observed in compounds **1**−**3**. There are two cations in the repeating unit of the helical strings. Two intermolecular hydrogen-bonding interactions are observed in compound **5**, in which the cations interact in a head-to-tail fashion, see Figure 5. In this case, the carbonyl oxygen interacts with both the amino hydrogens of tren and with those of the amino acidato ligand.

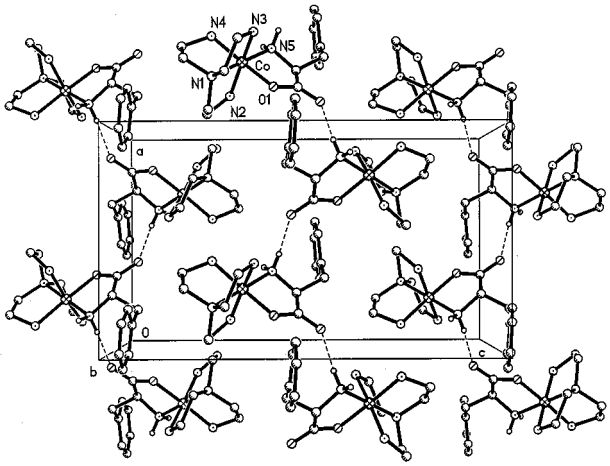

Figure 2. Spiral strings formed in compound **2**. Zigzag chains run along the *a* axis. When looking down along the *a* axis, phenyl rings wrap around the axis, instead of packing on top of each other as observed in compound **1**. Spiral strings run in space in ↑ ↓ fashion. Selected bond lengths: Co−O1 1.900(3), Co−N1 1.948(4), Co−N2 1.968(4), Co−N3 1.960(4), Co−N4 1.955(4), Co−N5 1.948(4) Å

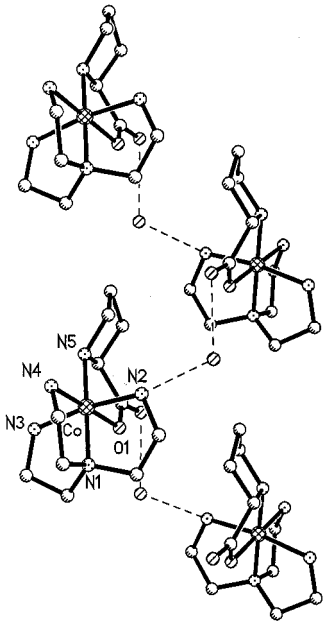

Figure 3. Spiral strings formed in compound **3**. The cations are "stitched" together by a water molecule, instead of direct cation-cation interaction. Selected bond lengths: Co−O1 1.900(3), Co−N1 1.960(5), Co−N2 1.965(5), Co−N3 1.974(5), Co−N4 1.956(5), Co−N5 1.959(5) Å

Compound **6**: Compound **6** contains helical strings running along the *b* axis with the typical head-to-tail hydrogen bonding observed in compound **5**, see Figure 6. In the reported racemic structure, a pair of head-to-head hydrogen bonds is formed between two complexes when the counter anions are iodides,[10b] whereas the perchlorate crystallizes in conglomerate solid solution, in the space group $P3_1$.[10c] A similar hydrogen-bonding motif is observed in the perchlorate complex as that in compound **6**, except that the

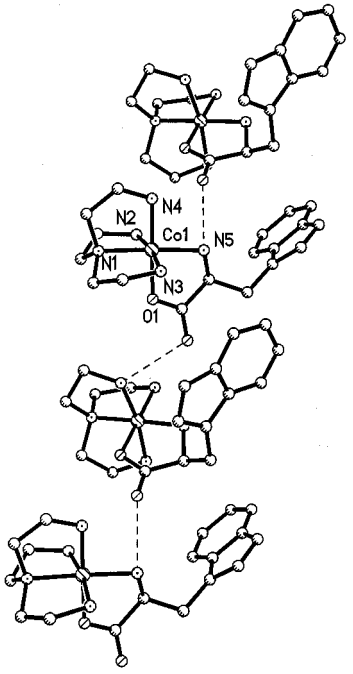

Figure 4. Spiral strings formed in compound **4**. There are two independent cations in the asymmetric unit and the conformation of the aromatic rings are slightly different. Selected bond lengths of Co1: Co1−O1 1.899(3), Co1−N1 1.949(5), Co1−N2 1.942(5), Co1−N3 1.957(5), Co1−N4 1.929(4), Co1−N5 1.952(4) Å

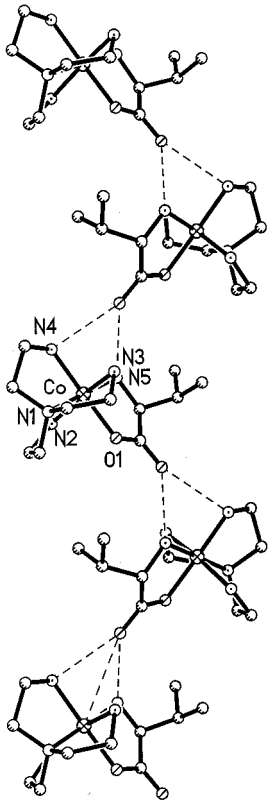

Figure 5. Spiral strings formed in compound **5**. Note that the hydrogen-bonding motif has been changed from single for the aromatic-substituted side chain to double for the aliphatic side chain. Selected bond lengths: Co−O1 1.921(3), Co−N1 1.949(4), Co−N2 1.953(4), Co−N3 1.968(4), Co−N4 1.940(4), Co−N5 1.948(4) Å

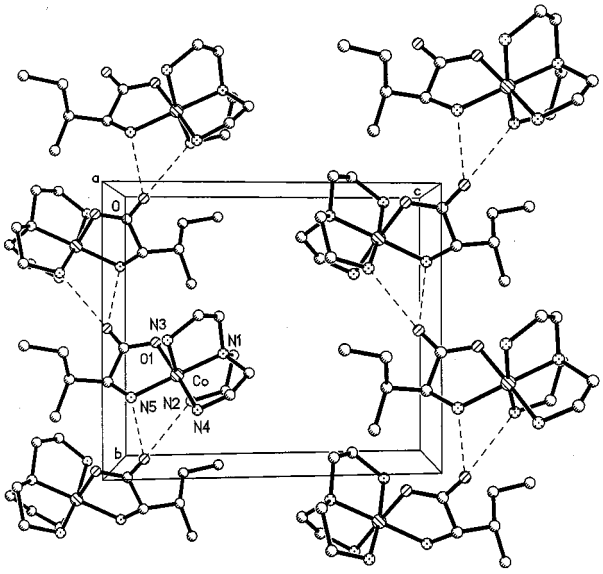

Figure 6. Spiral strings formed in compound **6**. Strings run in space in ↑ ↑ fashion. Selected bond lengths: Co−O1 1.906(4), Co−N1 1.943(5), Co−N2 1.974(5), Co−N3 1.984(6), Co−N4 1.935(5), Co−N5 1.940(5) Å

amino acidato groups in the different strings have different chirality.

Compound **7**: This compound crystallizes in the same unit cell, space group, and packing mode as the racemate reported previously.[10c] They make an interesting pair of optically active and racemic compounds that crystallize in the same space group with very similar packing properties. The racemic mixture is actually a conglomerate solid solution, in which the D and L form of the amino acidato group occupy alternative positions in the lattice. Interested readers are referred to the original copy for more detail.

Fundamental aspects of the packing modes adopted by the optically active and racemic species of [Co(tren)(amino acidato)]$^{2+}$ are the chiral helical strings observed in these systems:

(1) All helical strings are formed by intermolecular hydrogen bonds. In less bulky substituted amino acids such as valine, leucine, isoleucine, there are double hydrogen bonds; while with bulkier substituted amino acids such as phenylalanine, tryptophan, and proline, there are single hydrogen bonds. In both situations, the carbonyl oxygen atoms interact with the amino hydrogens of tren and/or with those of the amino acidato fragment.

(2) Hydrogen-bonding interactions can be very strong, as indicated by the favorable angles and distances. For instance, in compound **2**, the angle of N−H···O is 172° and N···O = 3.0 Å for the intermolecular hydrogen bond; while for **1**, the angle is 153° and the distance is 2.8 Å;

(3) Strings run in space either in a head-to-head ↑ ↑ fashion, as observed in compound **6**; or in a head-to-tail ↑ ↓ fashion, as observed in compound **2**;

(4) In the racemic form, helical strings have a similar packing mode as that observed in the optically active one, and intermolecular hydrogen-bonding interactions bring complexes of the same chirality together in those strings.

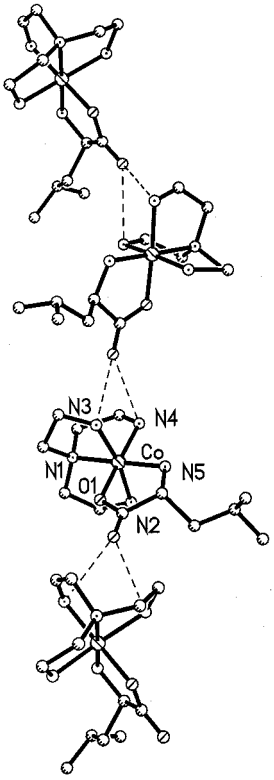

Figure 7. Spiral strings formed in compound **7**. The intermilecular hydroge-bonding interactions are the same as those observed in the racemic complex, except that the amino acidato ligands in different strings have different chirality in the racemic structure. Selected bond lengths: Co−O1 1.884(3), Co−N1 1.948(4), Co−N2 1.965(4), Co−N3 1.980(4), Co−N4 1.960(4), Co−N5 1.938(4) Å

However, the complexes of adjacent strings have opposite chirality. Since the hydrogen-bonding fashion observed in the racemic crystal is the same as that observed in the optically active form, we refer to it as the "chiral recognition motif" of these systems;

(5) Based upon our observations and understanding of conglomerate crystallization,[16] we can predict that [Co(tren)(amino acidato-*N*,*O*)]$^{2+}$ is a system that tends to favor conglomerate crystallization, if the "right stitching agents", (i.e. the counter anions and solvent), are chosen. This is consistent with the reported crystal structures of *trans*(*N*,*t*,*N*)-[Co(tren)(DL-leu)]I_2, *trans*(*N*,*t*,*N*)-[Co(tren)(DL-Ilu)]$(ClO_4)_2$, and *trans*(*N*,*t*,*N*)-[Co(tren) (DL-Val)]$(ClO_4)_2$.[10c]

1D and 2D ^{1}H NMR Spectra

In order to identify the individual protons, COSY spectra of compounds **1** to **4** were recorded. Individual peaks are resolved. Chemical shifts for the amino protons of tren range from δ = 3.92 to 5.09. It is difficult to assign chemical shifts for individual alkyl protons from the three different $N-CH_2-CH_2-NH_2$ arms. The spectra show that, for all four compounds, shifts from two arms are close, δ ≈ 2.9 and 3.3, while the others shift more upfield, δ ≈ 2.6 and 3.1. The upfield shifts are assigned to the arm that is *trans* to the carbonyl oxygen (referring to the coordinated position to Co^{III}). Interestingly, we observe that in the COSY

spectra of compound **4**, there are three cross peaks between three pairs of protons from the aromatic ring and the amino groups of tren; they are δ = 7.41 and 3.92, 7.13 and 4.18, 7.04 and 4.26, respectively. Based on the molecular structure shown in Figure 4, these protons are far away from each other and are not in parallel planes, therefore, there should not be any correlation. At present, we have no explanation for this long-range correlation.

Conclusion

It is interesting to note that chiral helical strings are formed among the cations $[Co(tren)(amino\ acidato)]^{2+}$, irrespective of the chirality and the nature of the substituted side chain of the amino acids. We hope that this observation will provide some information to further understand the chiral recognition processes that so readily occur in biological processes.

Experimental Section

All reagents were commercially available and used as received. − Elemental analyses were carried out with a Perkin−Elmer 240 elemental analyzer. − ^{1}H NMR spectra were recorded on a Varian UNITY/NOVA 500 NMR spectrometer using [D_6]DMSO as the solvent and TMS as the internal standard. A small amount of D_2O was added to the solution in order to assign the exchangeable protons after the spectra was recorded in [D_6]DMSO.

Safety Notes: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with great care.

Syntheses: Compounds were prepared according to the synthetic procedure originally described by Collman.[4] The pH of an aqueous solution of *cis*-α-[Co(tren)Cl_2]Cl (1.0 g, 0.003mol), was adjusted to 7.5−8.0 using freshly prepared 10% NaOH solution, whereupon the color of the solution changed to pink. An equimolar amount of amino acid was added while the pH was kept at 7.5−8.0. After heating at 60 °C for several hours in a water bath, the resulting solution was cooled to room temperature and filtered. Calculated amounts of KI or $NaClO_4$ were added to the resulting solution, and crystals suitable for X-ray diffraction were obtained after several days.

Elemental Analyses and ^{1}H NMR Spectroscopic Data

[Co(tren)(DL-phenylalaninato)]$(ClO_4)_2$ (1): $C_{15}H_{28}Cl_2CoN_5O_{10}$ (568.25): calcd. C 31.70, N 12.33, H 4.97; found C 30.20, N 12.60, H 4.81. Yield: 0.54 g, 30%.

[Co(tren)(L-phenylalaninato)]$I_2 \cdot H_2O$ (2): $C_{15}H_{30}CoI_2N_5O_3$ (641.17): calcd. C 28.01, N 10.93, H 4.72; found C 27.92, N 10.82, H 4.80. Yield: 0.74 g, 36%.

Compounds **1** and **2** have identical ^{1}H NMR: δ = 7.41 (d, ^3J = 8.0 Hz, 2 H, CH), 7.32 (d, ^3J = 7.5 Hz, 2 H, CH), 7.31 (t, ^3J = 9.0 Hz, 1 H, CH), 5.70 (t, ^3J = 8.0 Hz, 1 H, NH), 5.01 (m, 1 H, NH), 4.99 (m, 1 H, CH_2), 4.54 (t, ^3J = 10.0 Hz, 1 H, NH), 4.42 (m, 1 H, CH_2), 4.18 (m, 1 H, CH_2), 4.04 (m, 1 H, NH_2), 3.93 (m, 1 H, NH_2), 3.54 (m, 1 H, CH), 3.26−3.42 (m, 5 H, CH_2), 3.11 (t, ^3J = 7.5 Hz, 2 H, CH_2), 2.98 (m, 4 H, CH_2), 2.88 (dd, ^2J = 15 Hz, ^3J = 11.5 Hz, 1 H, CH_2), 2.66 (t, ^3J = 7.5 Hz, 2 H, CH_2).

[Co(tren)(L-prolinato)]$I_2 \cdot H_2O$ (3): $C_{11}H_{28}CoI_2N_5O_3$ (591.11): calcd. C 22.35, N 11.85, H 4.77, found C 22.51, N 10.79, H 4.70. − ^{1}H NMR: δ = 6.75 (m, 1 H, NH), 5.09 (m, 1 H, NH_2), 5.04 (m, 1 H, NH_2), 4.74 (m, 1 H, NH_2), 4.55 (m, 2 H, NH_2), 4.09 (m, 1 H, CH_2), 3.87 (d, ^3J = 9.0 Hz, 1 H, CH), 3.41 (m, 2 H, CH_2), 3.21 (m, 4 H, CH_2), 3.01 (dd, ^2J = 10 Hz, ^3J = 5.0 Hz, 1 H, CH_2), 2.93 (m, 3 H, CH_2), 2.72 (m, 2 H, CH_2), 2.43 (m, 1 H, CH_2), 2.14 (m, 1 H, CH_2), 1.96 (m, 1 H, CH_2), 1.89 (m, 1 H, CH_2), 1.74 (m, 1 H, CH_2). − Yield: 0.65 g, 34%.

[Co(tren)(L-tryptophanato)]$(ClO_4)_2 \cdot {}^1/_2H_2O$ (4): $C_{17}H_{31}Cl_2CoN_6O_{10.50}$ (617.30): calcd. C 33.04, N 13.60, H 5.02; found C, 35.91, N 11.42, H 5.97. − Yield: 0.72 g, 39%. − ^{1}H NMR: δ = 10.99 (s, 1 H, NH), 7.52 (d, ^3J = 8.0 Hz, 1 H, CH), 7.41 (d, ^3J = 7.5 Hz, 1 H, CH), 7.31 (d, ^3J = 2.0 Hz, 1 H, CH), 7.13 (td, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1 H, CH), 7.04 (td, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1 H, CH), 5.8 (m, 1 H, NH_2), 5.04 (m, 2 H, NH_2), 4.56 (m, 2 H, NH_2), 4.28 (m, 1 H, NH_2), 4.18 (m, 1 H, NH_2), 3.92 (m, 1 H, NH_2), 3.61 (m, 1 H, CH), 3.39 (m, 1 H, CH_2), 3.31 (m, 4 H, CH_2), 3.11 (t, ^3J = 6.0 Hz, 2 H, CH_2), 2.98 (m, 4 H, CH_2), 2.91 (m, 1 H, CH_2), 2.63 (t, ^3J = 6.0 Hz, 2 H, CH_2).

[Co(tren)(L-valinato)]$I_2 \cdot {}^1/_3H_2O$ (5): $C_{11}H_{28.67}CoI_2N_5O_{2.33}$ (581.06): calcd. C 22.71, N 12.04; H 4.93; found C, 23.89, N 12.58, H 5.32. − Yield: 0.71 g, 39%. − ^{1}H NMR: δ = 5.96 (t, J = 9.5 Hz, 1 H, NH_2), 5.03 (m, 1 H, NH_2), 4.73 (t, ^3J = 10.0 Hz, 1 H, NH_2), 4.50−4.40 (m, 3 H, NH_2), 4.18 (t, ^3J = 9.5 Hz, 1 H, NH_2), 3.98 (t, ^3J = 9.0 Hz, 1 H, NH_2), 3.42−3.30 (m, 4 H, CH_2), 3.24 (m, 3 H, CH_2, CH), 3.16−2.99 (m, 4 H, CH_2), 2.75 (brt, ^3J = 5.5 Hz, 2 H, CH_2), 2.21 (m, 1 H, CH_2), 1.09 (d, ^3J = 6.5 Hz, 3 H, CH_3), 0.93 (d, ^3J = 7.0 Hz, 3 H, CH_3).

[Co(tren)(L-isoleucinato)]I_2 (6): $C_{12}H_{30}CoI_2N_5O_2$ (589.14): calcd. C 24.46, N 11.19, H 5.13; found C 25.01, N 11.30, H 4.92. − Yield: 0.78 g, 41%. − ^{1}H NMR: δ = 6.01 (t, ^3J = 9.0 Hz, 1 H, NH_2), 5.05 (m, 1 H, NH_2), 4.74 (t, ^3J = 10.5 Hz, 1 H, NH_2), 4.49 (m, 2 H, NH_2), 4.38 (m, 1 H, NH_2), 4.21 (m, 1 H, NH_2), 3.98 (m, 1 H, NH_2), 3.43−3.27 (m, 5 H, CH_2, CH), 3.20 (m, 2 H, CH_2), 3.03−2.92 (m, 4 H, CH_2), 2.73 (m, 2 H, CH_2), 1.89 (m, 1 H, CH), 1.49 (m, 1 H, CH_2), 1.17 (m, 1 H, CH_2), 1.06 (d, ^3J = 7.0 Hz, 3 H, CH_3), 0.90 (t, ^3J = 7.5 Hz, 3 H, CH_3).

[Co(tren)(L-leucinato)]I_2 (7): $C_{12}H_{30}CoI_2N_5O_2$ (589.13): calcd. C 24.46, N 11.19, H 5.13, found C 25.21, N 11.53, H 4.98. − Yield: 0.66 g, 35%. − ^{1}H NMR: δ = 5.95 (t, ^3J = 9.5 Hz, 1 H, NH_2), 5.00 (m, 2 H, NH_2), 4.77 (t, ^3J = 10.0 Hz, 1 H, NH_2), 4.50 (m, 1 H, NH_2), 4.35 (m, 1 H, NH_2), 4.04 (m, 2 H, NH_2), 3.34 (m, 5 H, CH_2, CH), 3.15 (m, 2 H, CH_2), 3.01−2.94 (m, 4 H, CH_2), 2.72 (m, 2 H, CH_2), 1.85 (m, 2 H, CH), 1.61 (m, 2 H, CH_2), 0.99 (d, ^3J = 7.0 Hz, 3 H, CH_3), 0.94 (d, ^3J = 6.5 Hz, 3 H, CH_3).

X-ray Crystallography

Experimental details of the X-ray analyses are provided in Table 1 and Table 2. All diffraction data were collected on a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo-K_α radiation (λ= 0.71073 Å) at room temperature using the program SMART[17] and processed by SAINT+.[18] Absorption correction was applied by SADABS.[19]

Space groups of these compounds were determined from systematic absences and further justified by the results of refinement. In compound **1**, it was noted that the $|E^*E - 1| = 0.831$ and that systematic absences indicate that it crystallizes in the polar (non-centro-

Table 1. Crystallographic and experimental data for **1**−**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{15}H_{28}Cl_2CoN_5O_{10}$	$C_{15}H_{30}CoI_2N_5O_3$	$C_{11}H_{28}CoI_2N_5O_3$	$C_{17}H_{31}Cl_2CoN_6O_{10.5}$
Formula weight	568.25	641.17	591.11	617.31
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a [Å]	17.797(2)	10.1712(5)	9.0236(7)	11.1393(16)
b [Å]	11.7763(14)	12.6054(7)	10.9085(9)	18.459(3)
c [Å]	10.9053(14)	17.6765(10)	19.4365(15)	11.8131(16)
β [°]				94.003(3)
Volume [Å^3]	2285.6(5)	2266.3(2)	1913.2(3)	2423.2(6)
Z	4	4	4	4
Density (calc.) [g/m^3]	1.651	1.879	2.052	1.692
Absorption coefficient [mm^{-1}]	1.046	3.505	4.144	0.997
F(000)	1176	1248	1144	1280
Crystal size [mm]	0.5×0.2×0.2	0.3×0.15×0.13	0.4×0.2×0.2	0.25×0.15×0.15
Θ Range of data collection	2.07 to 27.03	2.14 to 27.00	1.98 to 27.07	1.73 to 27.08
reflections collected	7722	13806	6821	14836
Independent/observed refls [$I>2\sigma(I)$]	3340/2802	4960/4095	3701/3175	10062/5924
Transmission	0.8180−0.6227	0.6785−0.4195	0.4913−0.2881	0.8648−0.6912
Data/restraints/parameters	3340/1/316	4960/0/235	3701/0/199	10062/1/658
Goodness-of-fit on F^2	0.983	0.971	0.952	0.879
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.0415$	$R1 = 0.0303$	$R1 = 0.0367$	$R1 = 0.0496$
$wR2 = 0.1139$	$wR2 = 0.1139$	$wR2 = 0.0772$	$wR2 = 0.0795$	$wR2 = 0.0987$
R indices (all data)	$R1 = 0.0505$	$R1 = 0.0397$	$R1 = 0.0444$	$R1 = 0.0966$
$wR2 = 0.1094$	wR2 = 0.1094	$wR2 = 0.0801$	$wR2 = 0.0808$	$wR2 = 0.1101$

Table 2. Crystallographic and experimental data for **5**−**7**

Compound	**5**	**6**	**7**
Empirical formula	$C_{11}H_{28.7}CoI_2N_5O_{2.3}$	$C_{12}H_{30}CoI_2N_5O_2$	$C_{12}H_{30}CoI_2N_5O_2$
Formula weight	581.12	589.14	589.14
Crystal system	Orthorhombic	Monoclinic	Trigonal
Space group	$P2_12_12_1$	$P2_1$	$P3_2$
a [Å]	11.5598(6)	8.6576(7)	9.1653(5)
b [Å]	18.5803(10)	10.0933(8)	9.1653(5)
c [Å]	27.7747(16)	11.8068(9)	20.9419(16)
β [°]		98.1810(10)	
Volume [Å^3]	5965.6(6)	1021.22(14)	1523.49(17)
Z	12	2	3
Density(calc.) [g/m^3]	1.941	1.916	1.926
Absorption coefficient [mm^{-1}]	3.980	3.873	3.897
Crystal size mm	0.3×0.2×0.2	0.4×0.2×0.15	0.4×0.3×0.3
F(000)	3376	572	858
Θ Range of data collection	1.32 to 27.05	1.74 to 27.02	2.57 to 27.02
Reflections collected	21406	6115	5421
Independent/observed refls [$I>2\sigma(I)$]	12800/10282	3721/3485	3266/3046
Transmission	0.5032−0.3814	0.5940−0.3062	0.5095−0.3877
Data/restraints/parameters	12800/0/577	3721/1/194	3266/1/199
Goodness-of-fit on F^2	0.934	1.028	1.057
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.0316$	$R1 = 0.0406$	$R1 = 0.0263$
	$wR2 = 0.0591$	$wR2 = 0.1045$	$wR2 = 0.0658$
R indices (all data)	$R1 = 0.0456$	$R1 = 0.0433$	$R1 = 0.0291$
	$wR2 = 0.0620$	$wR2 = 0.1060$	$wR2 = 0.0666$

symmetric) space group $Pca2_1$, suggesting that phenylalanine racemizes during the synthetic procedure. In all cases, the structures were solved by direct methods and refined using full-matrix least-squares/difference Fourier techniques using SHELXTL.[20−22] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms of the ligands were then placed at idealized positions and refined as riding atoms with the relative isotropic parameters of the heavy atoms to which they are attached. Figure 1 through 7 show the cation conformations and packing feature of these complexes. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 141454 − CCDC 141460. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: (internat.) + 44−1233/336-033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This work is supported by the National Nature Science Foundation of China (No. 29801006), whom we thank for their generosity.

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Received March 8, 2000
[I00098]