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# The Structure of (+)-dinitrobis-(L-arginato)cobalt(III) Nitrate Dihydrate*

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*The structure and absolute configuration of (+)-dinitrobis-(L-arginato)cobalt(III) nitrate dihydrate was determined by single crystal X-ray diffraction techniques. The crystals belong to the triclinic space group P1 with unit cell dimensions of* $a = 11.250(5)$, $b = 9.867(5)$, $c = 5.701(8)$ Å, $\alpha = 89°(29)(5)'$, $\beta = 99°26(5)'$ *and* $\gamma = 93°13(15)'$. *The observed density of 1.588 g. cm*$^{-3}$ *is consistent with one formula unit per cell,* $d_c = 1.594$ *g. cm*$^{-3}$. *The anomalous dispersion of the cobalt(III) ion permitted the use of the Ps function to solve the structure directly. A total of 2044 independent reflections was collected by counter techniques and the model was refined to a conventional R index of 0.075 using the 1889 nonzero reflections. The crystal structure agrees with the R-configuration assigned by circular dichroism studies. The coordination around the cobalt(III) ion is distorted octahedral with the two nitro groups in a* cis *arrangement. The two amino acid ligands form five-membered chelate rings through use of the amino nitrogen and the carboxylate oxygen atoms; however, the conformations of the side chains differ. An extensive hydrogen bonding network exists in the solid state.*

## Introduction

Transition metal ions complexed with amino acids may serve as models for metal-protein interactions, and their structures may provide insight into the factors determining amino acid conformation. Generally, α-amino acids form five-membered chelate rings with the amino group and the carboxylate group acting as metal binding sites;[1] however, a number of amino acid side chain conformations have been observed. These variations may be attributed to extensive hydrogen bonding and packing interactions which exist in the solid state.

The structures of L-arginine dihydrate,[2] L-arginine monohydrobromide monohydrate,[3] L-arginine monohydrochloride monohydrate.[4] L-arginine monohydrochloride,[4] and L-arginine phosphate monohydrate[5] have been reported. The conformations of the side chains as well as bonding parameters for these molecules have been summarized in several reports.[4-7] The bond lengths and angles are consistent among each of the reported structures.

The chemical and physical properties of (+)-dinitrobis-(L-arginato)cobalt(III) nitrate have been reported[8] and solution circular dichroism studies were used to assign the configuration as R-. The crystal structure analysis of this complex was undertaken to confirm the absolute configuration, to determine the conformations of the extended carbon side chains and to determine if the guanidyl group also interacted with the metal ion. Interactions with the nitrogen of a folded side chain have been observed for a Cobalt(II) histidine complex,[9] and a bis-glycylglycinate-cobalt(III) complex.[10]

## Experimental Section

Reddish-brown crystals suitable for X-ray structural work were supplied by M. B. Celap and B. Kamberi. The following reaction describes the formation of the product:

$$\mathrm{Co(NO_3)_2 + 2\ L\text{-}argHCl\ (25\%\ KOH) + 2\ KNO_2} \longrightarrow$$
$$\mathrm{[Co(L\text{-}arg)_2(NO_2)_2]NO_3 \,.\, 2H_2O + other\ products}$$

The cobalt complex was purified by recrystallization from water. Carbon, nitrogen, hydrogen, and metal analyses were consistent with the formula $\mathrm{[Co(C_5N_4O_2H_{14})_2(NO_2)_2]NO_3 \cdot 2H_2O}$.

A crystal of dimensions 0.34 X 0.25 X 0.47 mm was used to collect all intensity data. The crystal was mounted with the long axis coincident with the spindle axis. The dimensions of the triclinic cell were determined at room temperature from $c$ axis rotation and hk0 Weissenberg photographs calibrated with NaCl powder lines using zirconium-filtered MoK$\alpha$ radiation, ($\lambda = 0.71069$ Å).

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(*) Contribution Number 8 from the FASTBIOS Labratory.

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Cristal data

$Co(C_6N_4O_2H_{14})_2(NO_2)_2NO_3 . 2H_2O$ $M = 597.4$
$a = 11.250(5)$ Å, $b = 9.867(5)$ Å, $c = 5.701(8)$ Å
$\alpha = 89°29(5)'$, $\beta = 99°26(5)'$, $\gamma = 93°13(5)'$

Space group: P1 (No systematic absences)

$Z = 1$; $V = 623.3$ Å$^3$; $\mu = 60.4$ cm$^{-1}$(CuK$\alpha$);
$d_o = 1.588$ g. cm$^{-3}$; $d_c = 1.594$ g. cm$^{-3}$

The errors in cell dimensions are standard deviations derived from the calculation of cell edges for a number of high angle reflections or layer lines. The errors in the angles are the average deviations obtained from several independent measurements of the same angle. The density was determined by the flotation method with a mixture of carbon tetrachloride and benzene.

Three-dimensional intensity data through the fourth level (hk4) were collected with a Phillips PAILRED diffractometer using equi-inclination geometry and the continuous ω-scan technique. The scan range varied from 3.4° for the zero level to 5.4° for the fourth level with a constant scan rate of 1°/min. Twenty second background counts were taken on either side of the peaks. CuK$\alpha$ radiation ($\lambda = 1.5418$ Å) and a graphite monochromator crystal [d(002) = 3.354 Å] were used to collect all the data. CuK$\alpha$ radiation was used because of the large correction to the imaginary part of the anomalous dispersion for cobalt ($\Delta f'' = 3.95$).[11] This was used to establish the absolute configuration. Several standard reflections were monitored throughout the data collection period. No statistically significant change in intensities was observed. The monitored reflections were used to scale the levels together.

In general, all of the nonequivalent reflections of the type hkl, $\bar{h}$kl, h$\bar{k}$l and $\bar{h}\bar{k}$l were collected up to a 2θ limit of 135°. A total of 2044 nonequivalent intensities was measured, and 1889 were tabulated as being observed, *i.e.* $I > 2\sigma(I)$. Friedel pairs were collected over a more limited range.

Lorentz and polarization corrections were applied to the data.[12] An absorption correction was made using a program for Weissenberg geometry.[13] The program is general and depends upon the equations of the crystal faces and not on the crystal class. The maximum and minimum transmission factors were calculated to be 0.344 and 0.166, respectively. Standard deviations were assigned on the basis of counting statics according to the equation

$$\sigma(F_o)^2 = \frac{A(N_s + RN_B + (0.03I_o)^2)}{4L_pI_o}$$

$$I_o = (N_s - RN_B)$$

where $N_s$ is the total count obtained during a scan cycle, $N_B$ is the total background count, R is a constant which relates the background count time to the total scan time, $I_o$ is the number of counts associated with each reflection, and A is the absorption correction.

The scattering factors of Cromer and Waber[14] were used for all nonhydrogen atoms. The scattering factor for cobalt(III) was corrected for the real and imaginary part of anomalous dispersion using the values of Cromer.[11] The hydrogen scattering factors were those calculated by Stewart, Davidson, and Simpson.[15]

## Structure Determination

There were large differences in the magnitudes of the Friedel pairs and the $P_s$ Patterson function of Pepinsky and Okaya[16] was used to solve the structure. Since one anomalous scatter exists per cell, the $P_s$ function yields the entire non-centrosymmetric distribution around the cobalt atom. All atoms in the two arginine ligands, the nitrate group and one of the $NO_2$ groups were located in the $P_s$ map. A structure factor calculation using 866 of the strongest reflections yielded a conventional R of 0.34 were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. Three cycles of block-diagonal least-squares using isotropic thermal parameters reduced the R value to 0.28. A three-dimensional Fourier map computed with the phases from the last least-squares calculation yielded all of the remaining nonhydrogen atoms. Reflections having $|F_o| > 2|F_c|$ were not used in the calculation.

All nonhydrogen atoms in the model were refined isotropically for 4 cycles using a block-diagonal least-squares program. The cobalt atom position was fixed at (1/2,1/2,1/2). The agreement factors for 866 reflections were R = .099 and R(wtd) = .099 where $R(wtd) = \Sigma w||F_o| - |F_c||/\Sigma w|F_o|$. The function minimized in the refinement is $\Sigma w(kF_o - F_c)^2$ where $w = [1/\sigma(F_o)]^2$.

Anisotropic thermal parameters were assigned to cobalt, the six atoms coordinated to the cobalt ion and the four oxygen atoms of the two coordinated nitro groups. Limited computer memory and expenses prevented a complete anisotropic refinement. Eight cycles of block-diagonal refinement reduced R to .057 and R(wtd) to .055 for the 866 reflections. The inclusion of anisotropic thermal parameters in the model was found to be significant at the $\alpha = 0.01$ level based on Hamilton's significance test.[17] Three cycles of full-matrix refinement were computed using 1299 reflections, and a three-dimensional difference Fourier map was calculated from the output. Most hydrogen atom positions could be assigned from the map. The positions of the hydrogen atoms associated with the water molecules are known with the least certainty. Three cycles of block-diagonal refinement yielded R = 0.0750 and R(wtd) = 0.0752 for all 1889 nonzero reflections. The contri-

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(12) A complete listing and description of all computer programs may be found in the Ph. D. dissertation of N. R. Stemple, Texas Christian University, 1970. The following programs written by N. R. Stemple were used in this investigation: Data Reduction, CDTRO; Fast Fourier (integer) FFOUR; Fourier, FR1ER; Full-Matrix Least-Squares (modification of a program written by Y. Okaya), CLSQ; Interatomic Distances and Angles, CDIST; and Structure Drawing, CDRAW.

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**Table I.** Squares of the observed and calculated structure factors for (+)-dinitrobis-(L-arginato)cobalt(III) nitrate dihydrate.

| H | FO$^2$ | FC$^2$ |
|---|---|---|
| K= | 11 | L= 0 |
| 2 | 58 | 67 |
| 1 | 37 | 47 |
| 0 | 184 | 182 |
| -1 | 56 | 58 |
| -2 | 17 | 27 |
| -3 | 7 | 20 |
| K= | 10 | L= 0 |
| 5 | 16 | 19 |
| 4 | 43 | 41 |
| 3 | ** | 1 |
| 2 | 26 | 22 |
| 1 | 91 | 90 |
| 0 | 83 | 67 |
| -1 | 70 | 70 |
| -2 | ** | 20 |
| -3 | 29 | 34 |
| -4 | 11 | 17 |
| -5 | ** | 9 |
| -6 | ** | 0 |
| K= | 9 | L= 0 |
| 7 | 73 | 64 |
| 6 | 92 | 105 |
| 5 | 87 | 95 |
| 4 | 59 | 47 |
| 3 | 105 | 111 |
| 2 | 22 | 35 |
| 1 | ** | 3 |
| 0 | 12 | 2 |
| -1 | 217 | 212 |
| -2 | ** | 4 |
| -3 | 97 | 104 |
| -4 | 93 | 67 |
| -5 | 70 | 52 |
| -6 | 13 | 33 |
| -7 | 96 | 96 |
| -8 | 7 | 13 |
| K= | 8 | L= 0 |
| 8 | 22 | 24 |
| 7 | 73 | 77 |
| 6 | 40 | 35 |
| 5 | ** | 16 |
| 4 | 30 | 41 |
| 3 | 18 | 34 |
| 2 | 29 | 11 |
| 1 | 502 | 487 |
| 0 | 507 | 607 |
| -1 | 270 | 290 |
| -2 | 580 | 638 |
| -3 | 172 | 176 |
| -4 | 56 | 77 |
| -5 | 21 | 32 |
| -6 | 16 | 23 |
| -7 | 21 | 16 |
| -8 | 16 | 22 |
| -9 | 37 | 36 |
| K= | 7 | L= 0 |
| 9 | 29 | 25 |
| 8 | 13 | 17 |
| 7 | 24 | 22 |
| 6 | 40 | 44 |
| 5 | 83 | 104 |
| 4 | 76 | 92 |
| 3 | 56 | 64 |
| 2 | 55 | 70 |
| 1 | 91 | 97 |
| 0 | 420 | 484 |
| -1 | 598 | 694 |
| -2 | 330 | 350 |
| -3 | 363 | 337 |
| -4 | 51 | 71 |
| -5 | 41 | 40 |
| -6 | 27 | 32 |
| -7 | ** | 1 |
| -8 | 8 | 15 |
| -9 | 32 | 32 |
| -10 | 16 | 20 |
| K= | 6 | L= 0 |
| 10 | 80 | 90 |
| 9 | 33 | 31 |
| 8 | 9 | 1 |
| 7 | 44 | 47 |
| 6 | 39 | 36 |
| 5 | 74 | 92 |
| 4 | 112 | 125 |
| 3 | 55 | 60 |
| 2 | 99 | 123 |
| 1 | 309 | 351 |
| 0 | 284 | 338 |
| -1 | 9 | 31 |
| -2 | 17 | 16 |
| -3 | 412 | 428 |
| -4 | 136 | 144 |
| -5 | 72 | 68 |
| -6 | 37 | 21 |
| -7 | 61 | 55 |
| -8 | 53 | 60 |
| -9 | 37 | 32 |
| -10 | 104 | 129 |
| -11 | 78 | 67 |
| K= | 5 | L= 0 |
| 11 | 14 | 12 |
| 10 | 75 | 89 |
| 9 | 104 | 136 |
| 8 | 73 | 73 |
| 7 | ** | 1 |
| 6 | 319 | 350 |
| 5 | 76 | 94 |
| 4 | 18 | 12 |
| 3 | 174 | 198 |
| 2 | 425 | 432 |
| 1 | 508 | 639 |
| 0 | 391 | 461 |
| -1 | 191 | 189 |
| -2 | 421 | 461 |
| -3 | 124 | 139 |
| -4 | 508 | 497 |
| -5 | 117 | 118 |
| -6 | 50 | 65 |
| -7 | 11 | 3 |
| -8 | ** | 3 |
| -9 | 185 | 182 |
| -10 | 201 | 203 |
| -11 | 57 | 54 |
| K= | 4 | L= 0 |
| 11 | ** | 0 |
| 10 | 27 | 37 |
| 9 | 15 | 5 |
| 8 | 122 | 123 |
| 7 | 96 | 108 |
| 6 | 147 | 153 |
| 5 | 401 | 408 |
| 4 | 1189 | 1369 |
| 3 | 1226 | 1576 |
| 2 | 377 | 406 |
| 1 | 340 | 429 |
| 0 | 256 | 366 |
| -1 | 276 | 401 |
| -2 | 892 | 909 |
| -3 | 4209 | 3380 |
| -4 | 1177 | 1310 |
| -5 | 378 | 378 |
| -6 | 180 | 189 |
| -7 | 297 | 298 |
| -8 | 80 | 81 |
| -9 | 30 | 17 |
| -10 | ** | 1 |
| -11 | 66 | 58 |
| -12 | 9 | 7 |
| K= | 3 | L= 0 |
| 12 | ** | 2 |
| 11 | 31 | 39 |
| 10 | 70 | 77 |
| 9 | 169 | 183 |
| 8 | 198 | 196 |
| 7 | 138 | 143 |
| 6 | 129 | 155 |
| 5 | 60 | 71 |
| 4 | 127 | 133 |
| 3 | 443 | 488 |
| 2 | 1593 | 1637 |
| 1 | 1706 | 1540 |
| 0 | 2184 | 1968 |
| -1 | 207 | 257 |
| -2 | 487 | 565 |
| -3 | 228 | 203 |
| -4 | 519 | 514 |
| -5 | 772 | 790 |
| -6 | 67 | 79 |
| -7 | 249 | 235 |
| -8 | 109 | 114 |
| -9 | ** | 0 |
| -10 | ** | 16 |
| -11 | 52 | 46 |
| -12 | ** | 0 |
| K= | 2 | L= 0 |
| 12 | 17 | 15 |
| 11 | 10 | 11 |
| 10 | 259 | 308 |
| 9 | 283 | 284 |
| 8 | 263 | 245 |
| 7 | 174 | 216 |
| 6 | 28 | 27 |
| 5 | 122 | 120 |
| 4 | 218 | 194 |
| 3 | 295 | 314 |
| 2 | 628 | 811 |
| 1 | 1274 | 1135 |
| 0 | 1274 | 1158 |
| -1 | 888 | 933 |
| -2 | 256 | 190 |
| -3 | 20 | 19 |
| -4 | 539 | 514 |
| -5 | 6 | 0 |
| -6 | 231 | 254 |
| -7 | 274 | 263 |
| -8 | 19 | 12 |
| -9 | 27 | 34 |
| -10 | 110 | 108 |
| -11 | 29 | 32 |
| -12 | 48 | 46 |
| K= | 1 | L= 0 |
| 12 | 26 | 20 |
| 11 | 60 | 58 |
| 10 | 165 | 159 |
| 9 | 163 | 181 |
| 8 | 197 | 174 |
| 7 | 73 | 89 |
| 6 | 76 | 80 |
| 5 | 9 | 4 |
| 4 | 131 | 120 |
| 3 | 1301 | 1177 |
| 2 | 1221 | 1068 |
| 1 | 2036 | 2000 |
| 0 | 1125 | 981 |
| -1 | 3363 | 3265 |
| K= | 1 | L= 0 |
| -2 | 1896 | 1551 |
| -3 | 6 | 17 |
| -4 | 716 | 757 |
| -5 | 278 | 319 |
| -6 | 562 | 603 |
| -7 | 61 | 62 |
| -8 | 76 | 100 |
| -9 | 134 | 140 |
| -10 | 73 | 76 |
| -11 | 16 | 8 |
| -12 | 22 | 13 |
| K= | 0 | L= 0 |
| 12 | 28 | 25 |
| 11 | 71 | 75 |
| 10 | 102 | 109 |
| 9 | 212 | 220 |
| 8 | 73 | 73 |
| 7 | 335 | 394 |
| 6 | 117 | 83 |
| 5 | 642 | 707 |
| 4 | 1102 | 1061 |
| 3 | 2476 | 1912 |
| 2 | 395 | 328 |
| 1 | 2147 | 1559 |
| -1 | 2267 | 1662 |
| -2 | 382 | 293 |
| -3 | 1782 | 1363 |
| -4 | 1854 | 1566 |
| -5 | 698 | 780 |
| -6 | 24 | 10 |
| -7 | 164 | 205 |
| -8 | 145 | 141 |
| -9 | 162 | 159 |
| -10 | 114 | 109 |
| -11 | 77 | 69 |
| -12 | 13 | 9 |
| K= | -1 | L= 0 |
| 12 | 10 | 5 |
| 11 | 9 | 6 |
| 10 | 41 | 38 |
| 9 | 70 | 62 |
| 8 | 94 | 120 |
| 7 | 58 | 37 |
| 6 | 478 | 512 |
| 5 | 284 | 290 |
| 4 | 855 | 880 |
| 3 | 76 | 59 |
| 2 | 2369 | 2037 |
| 1 | 3038 | 3088 |
| 0 | 1355 | 1147 |
| -1 | 2160 | 2090 |
| -2 | 1266 | 1090 |
| -3 | 791 | 778 |
| -4 | 56 | 50 |
| -5 | 11 | 19 |
| -6 | 42 | 53 |
| -7 | 74 | 89 |
| -8 | 235 | 231 |
| -9 | 151 | 159 |
| -10 | 219 | 193 |
| -11 | 59 | 52 |
| -12 | 12 | 8 |
| K= | -2 | L= 0 |
| 12 | 37 | 32 |
| 11 | 19 | 16 |
| 10 | 66 | 62 |
| 9 | 36 | 47 |
| 8 | 9 | 9 |
| 7 | 297 | 289 |
| 6 | 206 | 241 |
| 5 | 18 | 11 |
| 4 | 457 | 457 |
| 3 | 52 | 38 |
| 2 | 409 | 323 |
| 1 | 687 | 661 |
| 0 | 874 | 728 |
| -1 | 1390 | 1166 |
| -2 | 671 | 611 |
| -3 | 566 | 566 |
| -4 | 187 | 141 |
| -5 | 191 | 199 |
| -6 | 30 | 39 |
| -7 | 274 | 316 |
| -8 | 287 | 237 |
| -9 | 266 | 292 |
| -10 | 275 | 291 |
| -11 | 37 | 35 |
| -12 | 43 | 37 |
| K= | -3 | L= 0 |
| 12 | 10 | 8 |
| 11 | 47 | 42 |
| 10 | 30 | 51 |
| 9 | 27 | 25 |
| 8 | 110 | 130 |
| 7 | 347 | 337 |
| 6 | 182 | 213 |
| 5 | 670 | 669 |
| 4 | 344 | 350 |
| 3 | 330 | 271 |
| 2 | 250 | 263 |
| 1 | 67 | 75 |
| 0 | 1974 | 1660 |
| -1 | 2308 | 2045 |
| -2 | 1810 | 1756 |
| -3 | 294 | 274 |
| -4 | 234 | 242 |
| -5 | 51 | 65 |
| -6 | 241 | 273 |
| -7 | 148 | 150 |
| -8 | 169 | 155 |
| -9 | 133 | 138 |
| -10 | 115 | 110 |
| -11 | 69 | 65 |
| -12 | ** | 2 |
| K= | -4 | L= 0 |
| 12 | ** | 0 |
| 11 | 32 | 23 |
| 10 | 24 | 22 |
| 9 | 59 | 39 |
| 8 | 26 | 27 |
| 7 | 335 | 333 |
| 6 | 361 | 312 |
| 5 | 439 | 439 |
| 4 | 1299 | 1302 |
| 3 | 4653 | 3692 |
| 2 | 680 | 590 |
| 1 | 126 | 166 |
| 0 | 371 | 463 |
| -1 | 576 | 630 |
| -2 | 300 | 299 |
| -3 | 1664 | 1643 |
| -4 | 1102 | 1099 |
| -5 | 512 | 486 |
| -6 | 180 | 166 |
| -7 | 98 | 82 |
| -8 | 83 | 75 |
| -9 | ** | 5 |
| -10 | ** | 7 |
| -11 | 13 | 14 |
| K= | -5 | L= 0 |
| 11 | 67 | 70 |
| 10 | 169 | 158 |
| 9 | 197 | 189 |
| 8 | 30 | 30 |
| 7 | 40 | 28 |
| 6 | 28 | 36 |
| 5 | 275 | 279 |
| 4 | 317 | 296 |
| 3 | 35 | 30 |
| 2 | 422 | 425 |
| 1 | 179 | 144 |
| 0 | 314 | 330 |
| -1 | 696 | 734 |
| -2 | 569 | 497 |
| -3 | 336 | 319 |
| -4 | 70 | 64 |
| -5 | 211 | 235 |
| -6 | 273 | 271 |
| -7 | 14 | 21 |
| -8 | 13 | 18 |
| -9 | 50 | 64 |
| -10 | 82 | 89 |
| -11 | 35 | 27 |
| K= | -6 | L= 0 |
| 11 | 51 | 44 |
| 10 | 130 | 158 |
| 9 | 44 | 47 |
| 8 | 7 | 14 |
| 7 | 27 | 25 |
| 6 | 91 | 89 |
| 5 | 7 | 7 |
| 4 | 85 | 100 |
| 3 | 385 | 356 |
| 2 | 21 | 8 |
| 1 | 23 | 48 |
| 0 | 298 | 300 |
| -1 | 502 | 500 |
| -2 | 66 | 70 |
| -3 | 8 | 13 |
| -4 | 217 | 210 |
| -5 | 32 | 41 |
| -6 | 65 | 57 |
| -7 | 99 | 94 |
| -8 | 7 | 11 |
| -9 | 31 | 24 |
| -10 | 112 | 105 |
| K= | -7 | L= 0 |
| 10 | 28 | 29 |
| 9 | 11 | 10 |
| 8 | 27 | 22 |
| 7 | 14 | 13 |
| 6 | 20 | 11 |
| 5 | 35 | 38 |
| 4 | 32 | 59 |
| 3 | 451 | 401 |
| 2 | 458 | 440 |
| 1 | 620 | 638 |
| 0 | 397 | 370 |
| -1 | 163 | 157 |
| -2 | 38 | 44 |
| -3 | 73 | 61 |
| -4 | 70 | 64 |
| -5 | 78 | 84 |
| -6 | 54 | 50 |
| -7 | 49 | 46 |
| -8 | 33 | 36 |
| -9 | 46 | 32 |
| K= | -8 | L= 0 |
| 9 | 67 | 64 |
| 8 | 24 | 26 |
| 7 | ** | 0 |
| 6 | 44 | 31 |
| 5 | ** | 3 |
| 4 | 40 | 49 |
| 3 | 218 | 222 |
| K= | -8 | L= 0 |
| 2 | 666 | 650 |
| 1 | 311 | 291 |
| 0 | 706 | 723 |
| -1 | 496 | 394 |
| -2 | 123 | 82 |
| -3 | 16 | 14 |
| -4 | ** | 4 |
| -5 | 11 | 8 |
| -6 | ** | 2 |
| -7 | 65 | 64 |
| -8 | 52 | 51 |
| K= | -9 | L= 0 |
| 8 | 5 | 15 |
| 7 | 84 | 77 |
| 6 | 35 | 39 |
| 5 | 34 | 21 |
| 4 | 160 | 118 |
| 3 | 110 | 106 |
| 2 | 29 | 16 |
| 1 | 263 | 226 |
| 0 | 28 | 15 |
| -1 | 37 | 48 |
| -2 | 13 | 38 |
| -3 | 110 | 97 |
| -4 | 27 | 10 |
| -5 | 45 | 34 |
| -6 | 97 | 90 |
| -7 | 143 | 112 |
| K= | -10 | L= 0 |
| 6 | 5 | 8 |
| 5 | ** | 5 |
| 4 | ** | 1 |
| 3 | 16 | 15 |
| 2 | ** | 14 |
| 1 | 23 | 23 |
| 0 | 44 | 29 |
| -1 | 169 | 142 |
| -2 | ** | 6 |
| -3 | 25 | 25 |
| -4 | 61 | 51 |
| -5 | 19 | 17 |
| K= | -11 | L= 0 |
| 4 | 37 | 26 |
| 3 | 13 | 12 |
| 2 | 6 | 8 |
| 1 | 25 | 23 |
| 0 | 248 | 167 |
| -1 | 49 | 58 |
| -2 | 94 | 90 |
| K= | 11 | L= 1 |
| 2 | 97 | 89 |
| 1 | 6 | 12 |
| 0 | 12 | 10 |
| -1 | ** | 7 |
| -2 | 58 | 59 |
| -3 | 10 | 25 |
| -4 | 36 | 41 |
| K= | 10 | L= 1 |
| 5 | 5 | 6 |
| 4 | 11 | 11 |
| 3 | 78 | 77 |
| 2 | 90 | 71 |
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| 4 | 99 | 100 |
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| -2 | 169 | 165 |
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| 7 | 30 | 24 |
| 6 | 16 | 15 |
| 5 | 78 | 81 |
| 4 | 13 | 6 |
| 3 | 101 | 99 |
| 2 | 168 | 189 |
| 1 | 26 | 36 |
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| -2 | 337 | 328 |
| -3 | 51 | 63 |
| -4 | 155 | 149 |
| -5 | 82 | 82 |
| -6 | 38 | 59 |
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| -8 | 9 | 16 |
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| 8 | 13 | 13 |
| 7 | 41 | 42 |
| 6 | 47 | 49 |
| 5 | 113 | 122 |
| 4 | 43 | 38 |
| 3 | 12 | 17 |
| 2 | 36 | 38 |
| 1 | 339 | 349 |
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| -2 | 187 | 219 |
| -3 | 188 | 200 |
| -4 | 54 | 65 |
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| -9 | 26 | 42 |
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| K= | 6 | L= 1 |
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| 9 | 32 | 25 |
| 8 | 16 | 9 |
| 7 | 45 | 35 |
| 6 | 146 | 177 |
| 5 | 103 | 106 |
| 4 | 69 | 75 |
| 3 | 40 | 40 |
| 2 | 160 | 174 |
| 1 | 178 | 186 |
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| -2 | 539 | 554 |
| -3 | 595 | 518 |
| -4 | 78 | 80 |
| -5 | 235 | 270 |
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| -7 | 38 | 20 |
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| -9 | 48 | 48 |
| -10 | 50 | 69 |
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| 8 | 127 | 149 |
| 7 | 33 | 16 |
| 6 | 170 | 196 |
| 5 | 142 | 124 |
| 4 | 134 | 165 |
| 3 | 280 | 295 |
| 2 | 289 | 263 |
| 1 | 352 | 353 |
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| -2 | 139 | 141 |
| -3 | 229 | 267 |
| -4 | 183 | 208 |
| -5 | 96 | 107 |
| -6 | 87 | 95 |
| -7 | 112 | 126 |
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| 11 | ** | 3 |
| 10 | ** | 1 |
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| 8 | 114 | 143 |
| 7 | 168 | 146 |
| 6 | 258 | 292 |
| 5 | 1075 | 1348 |
| 4 | 229 | 197 |
| 3 | 195 | 204 |
| 2 | 91 | 103 |
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| -3 | 954 | 973 |
| -4 | 593 | 571 |
| -5 | 606 | 578 |
| -6 | 18 | 40 |
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| 9 | 46 | 45 |
| 8 | 136 | 130 |
| 7 | 162 | 169 |
| 6 | 97 | 104 |
| 5 | 526 | 561 |
| 4 | 1063 | 1177 |
| 3 | 258 | 249 |
| 2 | 239 | 223 |
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| K= | 2 | L= 1 |
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| 11 | 7 | 9 |
| 10 | 15 | 10 |
| 9 | 77 | 86 |
| 8 | 152 | 165 |
| 7 | 17 | 30 |
| 6 | 132 | 96 |
| 5 | 463 | 517 |
| 4 | 12 | 4 |
| 3 | 480 | 520 |
| 2 | 174 | 211 |
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| -2 | 937 | 817 |
| -3 | 151 | 123 |
| -4 | 133 | 169 |
| -5 | 1608 | 1567 |
| -6 | 446 | 392 |
| -7 | 314 | 345 |
| -8 | 140 | 141 |
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| -11 | 78 | 71 |
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| 12 | 63 | 27 |
| 11 | 8 | 9 |
| 10 | 35 | 24 |
| 9 | 153 | 211 |
| 8 | 76 | 89 |
| 7 | 282 | 365 |
| 6 | 398 | 462 |
| 5 | 64 | 46 |
| 4 | 714 | 704 |
| 3 | 684 | 816 |
| 2 | 7053 | 7428 |
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| -5 | 2171 | 1771 |
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| -7 | 149 | 140 |
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| K= | 0 | L= 1 |
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| 11 | 81 | 95 |
| 10 | 28 | 37 |
| 9 | 69 | 64 |
| 8 | 141 | 119 |
| 7 | 44 | 11 |
| 6 | 225 | 238 |
| 5 | 480 | 431 |
| 4 | 958 | 1135 |
| 3 | 537 | 635 |
| 2 | 13713 | 12907 |
| 1 | 904 | 649 |
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| -3 | 127 | 114 |
| -4 | 190 | 158 |
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| -6 | 64 | 75 |
| -7 | 48 | 47 |
| -8 | 38 | 37 |
| -9 | 95 | 103 |
| -10 | 14 | 16 |
| -11 | 19 | 21 |
| -12 | 13 | 13 |
| K= | -1 | L= 1 |
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| 11 | 9 | 1 |
| 10 | 11 | 5 |
| 9 | 40 | 34 |
| 8 | 291 | 271 |
| 7 | 216 | 190 |
| 6 | 380 | 342 |
| 5 | 205 | 178 |
| 4 | 106 | 115 |
| 3 | 377 | 381 |
| 2 | 1586 | 1446 |
| 1 | 94 | 127 |
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| -2 | 1451 | 1378 |
| -3 | 508 | 442 |
| -4 | 67 | 40 |
| -5 | 767 | 724 |
| -6 | 72 | 65 |
| -7 | 74 | 63 |
| -8 | 73 | 59 |
| -9 | 333 | 322 |
| -10 | 88 | 69 |
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| -12 | ** | 2 |
| K= | -2 | L= 1 |
| 12 | 18 | 11 |
| 11 | 19 | 11 |
| 10 | ** | 6 |
| 9 | 94 | 91 |
| 8 | 567 | 624 |
| 7 | 102 | 100 |
| 6 | 335 | 349 |
| 5 | 28 | 20 |
| 4 | 898 | 819 |
| 3 | 275 | 260 |
| 2 | 588 | 613 |
| 1 | 57 | 40 |
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| -1 | 616 | 594 |
| -2 | 3867 | 3465 |
| -3 | 1164 | 1055 |
| -4 | 1079 | 1039 |
| -5 | 641 | 637 |
| -6 | 206 | 208 |
| -7 | 148 | 156 |
| -8 | 296 | 297 |
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| -10 | 110 | 105 |
| -11 | 18 | 20 |
| -12 | 13 | 57 |
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| 12 | 4 | 13 |
| 11 | 24 | 16 |
| 10 | 45 | 52 |
| 9 | 46 | 34 |
| 8 | 232 | 189 |
| 7 | 377 | 368 |
| 6 | 145 | 98 |
| 5 | 67 | 81 |
| 4 | 461 | 435 |
| 3 | 198 | 213 |
| 2 | 365 | 357 |
| 1 | 111 | 65 |
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| -2 | 3428 | 3299 |
| -3 | 867 | 842 |
| -4 | 448 | 496 |
| -5 | 371 | 384 |
| -6 | 13 | 21 |
| -7 | 103 | 110 |
| -8 | 195 | 190 |
| -9 | 140 | 135 |
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| 10 | 17 | 13 |
| 9 | 114 | 112 |
| 8 | 154 | 117 |
| 7 | 340 | 377 |
| 6 | 308 | 269 |
| 5 | 1024 | 1036 |
| 4 | 36 | 40 |
| 3 | 54 | 81 |
| 2 | 155 | 165 |
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| -3 | 1801 | 1461 |
| -4 | 97 | 75 |
| -5 | 302 | 295 |
| -6 | 201 | 202 |
| -7 | 167 | 164 |
| -8 | 110 | 109 |
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| -10 | 48 | 68 |
| -11 | 34 | 56 |
| -12 | ** | 35 |
| K= | -5 | L= 1 |
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| 10 | 12 | 5 |
| 9 | ** | 5 |
| 8 | 140 | 138 |
| 7 | 64 | 80 |
| 6 | 96 | 101 |
| 5 | 66 | 59 |
| 4 | 183 | 190 |
| 3 | 209 | 162 |
| 2 | 229 | 234 |
| 1 | 11 | 31 |
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| -3 | 600 | 582 |
| -4 | 517 | 487 |
| -5 | 33 | 53 |
| -6 | 144 | 132 |
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| K= | -6 | L= 1 |
| 10 | ** | 1 |
| K= | -6 | L= 1 |
| 9 | 24 | 14 |
| 8 | 27 | 22 |
| 7 | ** | 1 |
| 6 | 36 | 36 |
| 5 | 68 | 68 |
| 4 | 16 | 11 |
| 3 | 49 | 46 |
| 2 | 348 | 371 |
| 1 | 412 | 427 |
| 0 | 275 | 293 |
| -1 | 153 | 179 |
| -2 | 385 | 357 |
| -3 | 94 | 122 |
| -4 | 225 | 231 |
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| -6 | 117 | 106 |
| -7 | 45 | 35 |
| -8 | 79 | 67 |
| -9 | 74 | 71 |
| -10 | 28 | 47 |
| K= | -7 | L= 1 |
| 10 | ** | 2 |
| 9 | 19 | 16 |
| 8 | ** | 3 |
| 7 | 70 | 52 |
| 6 | 104 | 83 |
| 5 | 170 | 141 |
| 4 | 40 | 36 |
| 3 | 219 | 203 |
| 2 | 473 | 414 |
| 1 | 163 | 149 |
| 0 | 267 | 280 |
| -1 | 210 | 196 |
| -2 | 212 | 205 |
| -3 | 169 | 166 |
| -4 | 322 | 280 |
| -5 | 120 | 118 |
| -6 | 106 | 109 |
| -7 | 56 | 50 |
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| K= | -8 | L= 1 |
| 9 | ** | 1 |
| 8 | 36 | 28 |
| 7 | 45 | 45 |
| 6 | 79 | 78 |
| 5 | 52 | 40 |
| 4 | 217 | 221 |
| 3 | 42 | 39 |
| 2 | 554 | 516 |
| 1 | 656 | 554 |
| 0 | 27 | 9 |
| -1 | 64 | 51 |
| -2 | 138 | 158 |
| -3 | 133 | 110 |
| -4 | 26 | 9 |
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| -6 | 54 | 71 |
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| -8 | 44 | 50 |
| K= | -9 | L= 1 |
| 7 | 45 | 52 |
| 6 | 64 | 65 |
| 5 | 53 | 55 |
| 4 | ** | 0 |
| 3 | 67 | 68 |
| 2 | 32 | 32 |
| 1 | ** | 17 |
| 0 | 69 | 60 |
| -1 | 170 | 157 |
| -2 | 31 | 37 |
| -3 | 80 | 73 |
| -4 | 89 | 77 |
| -5 | 72 | 55 |
| -6 | 16 | 26 |
| -7 | 98 | 89 |
| K= | -10 | L= 1 |
| 6 | 11 | 16 |
| 5 | 13 | 15 |
| 4 | 16 | 8 |
| 3 | 7 | 5 |
| 2 | 33 | 16 |
| 1 | 118 | 81 |
| 0 | 20 | 25 |
| -1 | 42 | 41 |
| -2 | 196 | 182 |
| -3 | 182 | 137 |
| -4 | 76 | 68 |
| -5 | 23 | 31 |
| K= | -11 | L= 1 |
| 3 | 13 | 11 |
| 2 | 70 | 60 |
| 1 | 41 | 36 |
| 0 | 93 | 87 |
| -1 | 126 | 125 |
| -2 | 61 | 69 |
| K= | 10 | L= 2 |
| 3 | 26 | 24 |
| 2 | 120 | 116 |
| 1 | 18 | 31 |
| 0 | 52 | 43 |
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| -2 | 33 | 25 |
| -3 | 10 | 6 |
| -4 | 39 | 40 |
| -5 | 56 | 58 |
| -6 | 17 | 53 |
| K= | 9 | L= 2 |
| 5 | 8 | 9 |
| 4 | 8 | 9 |
| 3 | 51 | 47 |
| 2 | 22 | 24 |
| 1 | 48 | 46 |
| 0 | 37 | 38 |
| -1 | 49 | 46 |
| -2 | 21 | 19 |
| -3 | 135 | 122 |
| -4 | 51 | 69 |
| -5 | 12 | 23 |
| -6 | 110 | 122 |
| -7 | 94 | 103 |
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| K= | 8 | L= 2 |
| 7 | 11 | 9 |
| 6 | 6 | 10 |
| 5 | 33 | 37 |
| 4 | 80 | 76 |
| 3 | 67 | 70 |
| 2 | 106 | 100 |
| 1 | 108 | 109 |
| 0 | 240 | 244 |
| -1 | 32 | 31 |
| -2 | 126 | 124 |
| -3 | 62 | 61 |
| -4 | 134 | 135 |
| -5 | ** | 21 |
| -6 | 125 | 131 |
| -7 | 20 | 50 |
| -8 | 21 | 36 |
| -9 | ** | 6 |
| K= | 7 | L= 2 |
| 8 | ** | 7 |
| 7 | 14 | 13 |
| 6 | 58 | 55 |
| 5 | 31 | 35 |
| 4 | 103 | 85 |
| 3 | 157 | 153 |
| 2 | 390 | 381 |
| 1 | 136 | 138 |
| 0 | 103 | 106 |
| -1 | 49 | 81 |
| -2 | 39 | 39 |
| -3 | 9 | 2 |
| -4 | ** | 6 |
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| -6 | 57 | 52 |
| -7 | 195 | 210 |
| -8 | 108 | 97 |
| -9 | 45 | 53 |
| -10 | ** | 16 |
| K= | 6 | L= 2 |
| 9 | 5 | 7 |
| 8 | 14 | 12 |
| 7 | 37 | 31 |
| 6 | 97 | 85 |
| 5 | 37 | 33 |
| 4 | 178 | 176 |
| 3 | 173 | 152 |
| 2 | 19 | 11 |
| 1 | 311 | 328 |
| 0 | 335 | 327 |
| -1 | 248 | 218 |
| -2 | 137 | 140 |
| -3 | 169 | 210 |
| -4 | 513 | 418 |
| -5 | 33 | 18 |
| -6 | 415 | 354 |
| -7 | 85 | 108 |
| -8 | 135 | 164 |
| -9 | 79 | 75 |
| -10 | 49 | 110 |
| -11 | ** | 31 |
| K= | 5 | L= 2 |
| 10 | 17 | 13 |
| 9 | 16 | 9 |
| 8 | 22 | 20 |
| 7 | 25 | 2 |
| 6 | 103 | 93 |
| 5 | 170 | 180 |
| 4 | 189 | 181 |
| 3 | 140 | 120 |
| 2 | 519 | 544 |
| 1 | 31 | 34 |
| 0 | 104 | 96 |
| -1 | 35 | 30 |
| -2 | 52 | 59 |
| -3 | 315 | 351 |
| -4 | 431 | 434 |
| -5 | 17 | 17 |
| -6 | 261 | 261 |
| -7 | 611 | 604 |
| -8 | 319 | 315 |
| -9 | 14 | 35 |
| -10 | 47 | 54 |
| -11 | 5 | 19 |
| -12 | ** | 26 |
| K= | 4 | L= 2 |
| 10 | 25 | 26 |
| 9 | 28 | 7 |
| 8 | 43 | 30 |
| 7 | 247 | 283 |
| 6 | 169 | 173 |
| 5 | 156 | 158 |
| 4 | 273 | 254 |
| 3 | 378 | 413 |
| K= | 4 | L= 2 |
| 2 | 55 | 41 |
| 1 | 30 | 48 |
| 0 | 140 | 127 |
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| -2 | 228 | 269 |
| -3 | 484 | 749 |
| -4 | 414 | 461 |
| -5 | 247 | 246 |
| -6 | 61 | 49 |
| -7 | 43 | 70 |
| -8 | 351 | 338 |
| -9 | 153 | 164 |
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| -12 | ** | 5 |
| K= | 3 | L= 2 |
| 11 | 9 | 8 |
| 10 | 21 | 9 |
| 9 | 66 | 50 |
| 8 | 45 | 30 |
| 6 | 140 | 154 |
| 5 | 23 | 13 |
| 4 | 376 | 354 |
| 3 | 335 | 295 |
| 2 | 22 | 30 |
| 1 | 77 | 82 |
| 0 | 2 | 8 |
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| -2 | 425 | 413 |
| -3 | 764 | 953 |
| -4 | 1191 | 1171 |
| -5 | 310 | 296 |
| -6 | 108 | 108 |
| -7 | 78 | 85 |
| -8 | 44 | 30 |
| -9 | 94 | 63 |
| -10 | 77 | 64 |
| -11 | 7 | 15 |
| -12 | 21 | 58 |
| K= | 2 | L= 2 |
| 11 | 19 | 10 |
| 10 | 54 | 41 |
| 9 | ** | 2 |
| 8 | 14 | 18 |
| 7 | 91 | 63 |
| 6 | 53 | 113 |
| 5 | 39 | 36 |
| 4 | 1097 | 1364 |
| 3 | 758 | 795 |
| 2 | 122 | 145 |
| 1 | 1147 | 1136 |
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| -6 | 661 | 623 |
| -7 | 398 | 413 |
| -8 | 143 | 183 |
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| -12 | 27 | 42 |
| K= | 1 | L= 2 |
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| 10 | 16 | 10 |
| 9 | 18 | 17 |
| 8 | 28 | 53 |
| 7 | ** | 10 |
| 6 | 114 | 117 |
| 5 | 499 | 649 |
| 4 | 880 | 1254 |
| 3 | 1328 | 1301 |
| 2 | 1617 | 1639 |
| 1 | 316 | 308 |
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| K= | 0 | L= 2 |
| 11 | 39 | 46 |
| 10 | 16 | 7 |
| 9 | ** | 5 |
| 8 | 31 | 50 |
| 7 | 62 | 41 |
| 6 | 141 | 149 |
| 5 | 35 | 107 |
| 4 | 1219 | 1281 |
| 3 | 2481 | 2183 |
| 2 | 1454 | 1311 |
| 1 | 1743 | 1466 |
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| -6 | 554 | 447 |
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| -10 | 88 | 85 |
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| -12 | 7 | 6 |
| K= | -1 | L= 2 |
| 11 | ** | 0 |
| 10 | 13 | 21 |
| 9 | ** | 0 |
| 8 | 19 | 29 |
| 7 | 187 | 162 |
| 6 | 135 | 130 |
| 5 | 181 | 163 |
| 4 | 812 | 870 |
| 3 | 849 | 701 |
| 2 | 2568 | 2115 |
| 1 | 2299 | 2071 |
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| -3 | 253 | 187 |
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| -5 | 769 | 601 |
| -6 | 36 | 51 |
| -7 | 1479 | 1317 |
| -8 | 548 | 488 |
| -9 | 305 | 297 |
| -10 | 9 | 9 |
| -11 | ** | 6 |
| -12 | ** | 2 |
| K= | -2 | L= 2 |
| 11 | 8 | 10 |
| 10 | 30 | 37 |
| 9 | 13 | 16 |
| 8 | 90 | 99 |
| 7 | 321 | 313 |
| 6 | 213 | 179 |
| 5 | 169 | 127 |
| 4 | 66 | 100 |
| 3 | 512 | 448 |
| 2 | 51 | 53 |
| 1 | 132 | 135 |
| 0 | 461 | 363 |
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| -2 | 98 | 53 |
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| -4 | 887 | 822 |
| -5 | 632 | 603 |
| -6 | 900 | 857 |
| -7 | 693 | 672 |
| -8 | 396 | 353 |
| -9 | 45 | 41 |
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| -11 | 57 | 51 |
| -12 | 7 | 4 |
| K= | -3 | L= 2 |
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| 9 | 48 | 43 |
| 8 | 56 | 36 |
| 7 | 317 | 322 |
| 6 | 330 | 275 |
| 5 | 71 | 58 |
| 4 | 263 | 231 |
| 3 | 215 | 192 |
| 2 | 347 | 345 |
| 1 | 191 | 167 |
| 0 | 679 | 616 |
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| -2 | 636 | 636 |
| -3 | 613 | 596 |
| -4 | 57 | 35 |
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| -7 | 607 | 549 |
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| -11 | 16 | 15 |
| -12 | ** | 8 |
| K= | -4 | L= 2 |
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| 10 | 27 | 29 |
| 9 | 11 | 10 |
| 8 | 28 | 14 |
| 7 | 312 | 347 |
| 6 | 288 | 222 |
| 5 | 176 | 151 |
| 4 | 223 | 205 |
| 3 | 56 | 48 |
| 2 | 27 | 21 |
| 1 | 22 | 21 |
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| -2 | 70 | 51 |
| -3 | 857 | 838 |
| -4 | 212 | 197 |
| -5 | 121 | 105 |
| -6 | 81 | 50 |
| -7 | 109 | 106 |
| -8 | 133 | 117 |
| -9 | 121 | 104 |
| -10 | 20 | 24 |
| -11 | 29 | 30 |
| K= | -5 | L= 2 |
| 10 | 28 | 24 |
| 9 | 21 | 15 |
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| 8 | ** | 1 |
| 7 | ** | 4 |
| 6 | 276 | 227 |
| 5 | 216 | 170 |
| 4 | 125 | 94 |
| 3 | 127 | 127 |
| 2 | ** | 8 |
| 1 | 327 | 320 |
| 0 | 572 | 538 |
| -1 | 277 | 247 |
| -2 | 407 | 306 |
| -3 | 231 | 223 |
| -4 | 621 | 520 |
| -5 | 88 | 84 |
| -6 | 163 | 159 |
| -7 | 14 | 16 |
| -8 | 58 | 63 |
| -9 | 15 | 12 |
| -10 | 40 | 36 |
| -11 | 106 | 103 |
| K= | -6 | L= 2 |
| 10 | 5 | 19 |
| 9 | 12 | 13 |
| 8 | 13 | 15 |
| 7 | 11 | 8 |
| 6 | 172 | 153 |
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| 5 | 239 | 197 |
| 4 | 299 | 239 |
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| 6 | 113 | 110 |
| 5 | 86 | 30 |
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| 3 | 321 | 305 |
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| 6 | 19 | 18 |
| 5 | 31 | 30 |
| 4 | 96 | 114 |
| 3 | 37 | 42 |
| 2 | 36 | 35 |
| 1 | 140 | 111 |
| 0 | 22 | 25 |
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| -2 | 25 | 38 |
| -3 | 193 | 155 |
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| -5 | 116 | 65 |
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| K= | -10 | L= 2 |
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| 4 | 6 | 2 |
| 3 | 18 | 22 |
| 2 | 27 | 28 |
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| 6 | 7 | 3 |
| 5 | ** | 0 |
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| 3 | 22 | 20 |
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| 5 | 17 | 13 |
| 4 | 85 | 90 |
| 3 | ** | 5 |
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| 7 | ** | 0 |
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| 5 | 82 | 75 |
| 4 | 43 | 48 |
| 3 | 99 | 114 |
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| 9 | 8 | 0 |
| 8 | 21 | 11 |
| 7 | ** | 3 |
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| 5 | 13 | 6 |
| 4 | 123 | 131 |
| 3 | 14 | 6 |
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| -5 | 145 | 152 |
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| 8 | 39 | 46 |
| 7 | 17 | 20 |
| 6 | 43 | 48 |
| 5 | 27 | 30 |
| 4 | 91 | 90 |
| 3 | ** | 25 |
| K= | 4 | L= 3 |
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| 1 | 115 | 106 |
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| -4 | 231 | 240 |
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| -7 | 309 | 277 |
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| 9 | 12 | 1 |
| 8 | 99 | 112 |
| 7 | 21 | 15 |
| 6 | 36 | 39 |
| 5 | 120 | 128 |
| 4 | 65 | 39 |
| 3 | 14 | 5 |
| 2 | 172 | 145 |
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| -5 | 125 | 122 |
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| 9 | 58 | 64 |
| 8 | 9 | 3 |
| 7 | 9 | 27 |
| 6 | 269 | 384 |
| 5 | 79 | 72 |
| 4 | 19 | 5 |
| 3 | 227 | 237 |
| 2 | 89 | 89 |
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| -2 | 22 | 26 |
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| -5 | 494 | 490 |
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| K= | 1 | L= 3 |
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| 9 | 44 | 9 |
| 8 | 15 | 25 |
| 7 | 116 | 194 |
| 6 | 67 | 126 |
| 5 | 32 | 11 |
| 4 | 151 | 139 |
| 3 | 12 | 6 |
| 2 | 312 | 285 |
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| 7 | 18 | 56 |
| 6 | 37 | 61 |
| 5 | 184 | 150 |
| 4 | 240 | 295 |
| 3 | 119 | 153 |
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| 9 | 30 | 24 |
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| 7 | 18 | 6 |
| 6 | 104 | 124 |
| 5 | 74 | 55 |
| 4 | 252 | 293 |
| 3 | 438 | 415 |
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| 5 | 123 | 113 |
| 4 | ** | 12 |
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| 9 | 47 | 47 |
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| 7 | 18 | 7 |
| 6 | 36 | 30 |
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| 8 | ** | 29 |
| 7 | ** | 2 |
| 6 | ** | 8 |
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| 4 | 115 | 90 |
| 3 | 71 | 68 |
| 2 | 346 | 326 |
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| -7 | 53 | 68 |
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| 6 | 39 | 46 |
| 5 | 29 | 15 |
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| 3 | 84 | 74 |
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| 3 | 18 | 27 |
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| 5 | 38 | 37 |
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| 7 | 11 | 3 |
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| 5 | ** | 12 |
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| 3 | 15 | 47 |
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| 7 | 43 | 46 |
| 6 | 31 | 23 |
| 5 | ** | 16 |
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| 3 | 65 | 66 |
| 2 | 80 | 108 |
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| 4 | 76 | 67 |
| 3 | 82 | 84 |
| 2 | 99 | 90 |
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| 0 | 131 | 103 |
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| 3 | 88 | 69 |
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| 4 | 194 | 244 |
| 3 | 153 | 162 |
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| 4 | 53 | 36 |
| 3 | 158 | 147 |
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| 6 | 27 | 14 |
| 5 | 15 | 30 |
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| 3 | 76 | 54 |
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| 3 | 50 | 52 |
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| 5 | 20 | 22 |
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| 3 | 35 | 36 |
| 2 | 9 | 6 |
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| -3 | 57 | 48 |
| -4 | 50 | 54 |

Thermal parameters are of the form $\exp -0.25(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)$.

| Atom | X | Y | Z | $B_{11}$ [a] | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | .5000 | .5000 | .5000 | 3.5 | 1.7 | 3.4 | 0.0 | 2.0 | 0.3 |
| O(1) | .3983(4) | .4925(4) | .1969(5) | 3.7 | 2.9 | 3.6 | 0.0 | 0.7 | —0.1 |
| N(1) | .3730(5) | .5959(6) | .6059(14) | 4.1 | 2.2 | 3.7 | —0.5 | 0.8 | —0.2 |
| O(1′) | .4191(3) | .3385(4) | .5963(5) | 3.6 | 2.7 | 2.9 | 0.0 | 1.9 | 0.2 |
| N(1′) | .6104(5) | .3742(6) | .3910(10) | 2.9 | 2.4 | 2.6 | 0.8 | 1.3 | 0.1 |
| N(6) | .5868(7) | .6566(7) | .3422(10) | 3.7 | 3.1 | 3.1 | —0.4 | 0.1 | 0.0 |
| O(6) | .5307(5) | .7585(6) | .3442(11) | 2.9 | 3.9 | 6.9 | —0.4 | 3.1 | 1.2 |
| O(7) | .6945(4) | .6594(5) | .4211(9) | 3.7 | 4.6 | 5.4 | —1.5 | 0.1 | 1.4 |
| N(6′) | .5967(7) | .5141(10) | .8145(12) | 4.3 | 5.7 | 1.8 | —1.4 | 1.0 | —1.1 |
| O(6′) | .6589(6) | .4232(8) | .8925(7) | 7.2 | 6.7 | 3.5 | 2.5 | —0.1 | 0.9 |
| O(7′) | .5891(5) | .6163(8) | .9201(9) | 6.3 | 7.7 | 3.5 | —1.7 | 1.5 | —2.2 |
| C(1) | .2894(5) | .5169(7) | .2043(14) | 2.6 | | | | | |
| O(2) | .2090(4) | .4998(5) | .0206(7) | 3.8 | | | | | |
| C(2) | .2580(6) | .5667(7) | .4357(14) | 2.9 | | | | | |
| C(3) | .1770(7) | .6927(9) | .4022(20) | 3.9 | | | | | |
| C(4) | .2278(7) | .7973(10) | .2436(20) | 4.4 | | | | | |
| C(5) | .1690(6) | .9338(8) | .2478(16) | 3.2 | | | | | |
| N(2) | .2176(5) | .0189(6) | .0718(7) | 3.5 | | | | | |
| C(6) | .1947(6) | .1500(7) | .0388(17) | 3.0 | | | | | |
| N(3) | .2469(4) | .2213(6) | —.1148(10) | 3.5 | | | | | |
| N(4) | .1235(5) | .2093(7) | .1679(11) | 3.8 | | | | | |
| C(1′) | .4502(5) | .2322(7) | .5182(17) | 2.6 | | | | | |
| O(2′) | .4092(3) | .1184(5) | .5717(8) | 4.0 | | | | | |
| C(2′) | .5398(6) | .2438(7) | .3380(15) | 2.8 | | | | | |
| C(3′) | .6147(6) | .1207(8) | .3448(17) | 3.3 | | | | | |
| C(4′) | .6868(7) | .1163(8) | .1379(17) | 3.6 | | | | | |
| C(5′) | .7445(7) | —.0209(9) | .1458(17) | 3.9 | | | | | |
| N(2′) | .8202(4) | —.0305(6) | —.0341(8) | 2.9 | | | | | |
| C(6′) | .8651(6) | —.1442(8) | —.0850(14) | 3.0 | | | | | |
| N(3′) | .9366(5) | —.1453(6) | —.2543(10) | 3.7 | | | | | |
| N(4′) | .8430(5) | —.2606(7) | .0290(15) | 4.2 | | | | | |
| N(5) | .9460(5) | .2253(7) | .5832(9) | 4.0 | | | | | |
| O(3) | .9841(3) | .1166(5) | .5292(10) | 4.5 | | | | | |
| O(4) | .8742(5) | .2267(7) | .7252(13) | 6.6 | | | | | |
| O(5) | .9789(6) | .3310(8) | .4963(13) | 6.9 | | | | | |
| O(8) | .9811(6) | .5645(7) | .7873(11) | 6.2 | | | | | |
| O(9) | .4064(4) | .8819(6) | .8417(9) | 5.4 | | | | | |

Hydrogen atoms parameters. Temperature factor of 3.0 assigned to all atoms.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H(1) | .394 | .695 | .608 | H(1′) | .680 | .361 | .521 |
| H(2) | .362 | .564 | .767 | H(2′) | .637 | .411 | .243 |
| H(3) | .208 | .482 | .499 | H(3′) | .484 | .250 | .168 |
| H(4) | .175 | .737 | .572 | H(4′) | .675 | .118 | .510 |
| H(5) | .087 | .660 | .324 | H(5′) | .557 | .030 | .343 |
| H(6) | .323 | .812 | .298 | H(6′) | .756 | .196 | .158 |
| H(7) | .214 | .760 | 064 | H(7′) | .627 | .126 | —.027 |
| H(8) | .194 | .979 | .420 | H(8′) | .797 | —.035 | .318 |
| H(9) | .073 | .919 | .197 | H(9′) | .675 | —.101 | .121 |
| H(10) | .273 | .976 | —.033 | H(10′) | .840 | .056 | —.127 |
| H(11) | .238 | .320 | —.129 | H(11′) | .953 | —.061 | —.342 |
| H(12) | .296 | .175 | —.217 | H(12′) | .973 | —.230 | —.290 |
| H(13) | .114 | .308 | .155 | H(13′) | .790 | —.262 | .151 |
| H(14) | .080 | .154 | .276 | H(14′) | .880 | —.345 | —.009 |
| H(15) | .407 | .959 | .754 | H(17) | .055 | .544 | .863 |
| H(16) | .460 | .544 | .863 | H(18) | .960 | .476 | .696 |

[a] The average standard deviation for the thermal parameters is approximately 0.3.

butions of the hydrogen atoms were calculated, but the parameters were not refined. Generally, those reflections assigned a zero magnitude have a calculated magnitude less than the observed minimum. The final observed and calculated structure factors for all 2044 reflections are included in Table I.

All shifts of the parameters for nonhydrogen atoms during the final cycle of refinement were less than one-seventh of the estimated standard deviations of the parameters. The final positional and thermal parameters along with their estimated standard deviations are given in Table II. A final three-dimensional difference Fourier map was calculated and no peak was larger than those associated with hydrogen atoms. Structure factor calculations for the Friedel pairs indicated the correct configuration has been assigned.

## Discussion

Figure 1 shows a projection of the contents of the unit cell onto the *ab* plane. Both arginine ligands are bidentate and coordinate to the cobalt through the

**Table III.** Interatomic distances and bond angles for (+)-dinitrobis-(L-arginato)cobalt(III)nitrate dihydrate.

| | | | |
|---|---|---|---|
| Co-O(1) | 1.909(3)Å | Co-O(1') | 1.912(4) |
| Co-N(1) | 1.935(6) | Co-N(1') | 1.977(6) |
| O(1)-C(1) | 1.270(8) | O(1')-C(1') | 1.234(8) |
| C(1)-O(2) | 1.272(9) | C(1')-O(2') | 1.244(8) |
| C(1)-C(2) | 1.513(10) | C(1')-C(2') | 1.552(11) |
| C(2)-N(1) | 1.501(10) | C(1')-N(1') | 1.480(9) |
| C(2)-C(3) | 1.574(11) | C(2')-C(3') | 1.514(11) |
| C(3)-C(4) | 1.519(13) | C(3')-C(4') | 1.539(13) |
| C(4)-C(5) | 1.535(11) | C(4')-C5') | 1.531(12) |
| C(5)-N(2) | 1.458(9) | C(5')-N(2') | 1.444(10) |
| N(2)-C(6) | 1.339(9) | N(2')-C(6') | 1.310(9) |
| C(6)-N(3) | 1.311(10) | C(6')-N(3') | 1.354(9) |
| C(6)-N(4) | 1.333(9) | C(6')-N(4') | 1.355(10) |
| Co-N(6) | 1.894(7) | Co-N(6') | 1.941(7) |
| N(6)-O(6) | 1.240(9) | N(6')-O(6') | 1.205(11) |
| N(6)-O(7) | 1.201(9) | N(6')-O(7') | 1.194(12) |
| N(5)-O(3) | 1.236(8) | N(5)-O(4) | 1.235(9) |
| N(5)-O(6) | 1.216(10) | | |
| O(1)CoN(1) | 85.8(2)° | N(1)CoN(6) | 96.0(3) |
| O(1)CoN(1') | 91.1(2) | O(1')CoN(1') | 84.7(2) |
| O(1)CoO(1') | 90.4(2) | O(1')CoN(6') | 89.7(3) |
| O(1)CoN(6) | 91.4(2) | N(1)'CoN(6') | 92.2(3) |
| N(1)CoO(1') | 86.0(2) | N(1')CoN(6) | 93.5(3) |
| N(1)CoN(6') | 90.9(3) | N(6')CoN(6) | 88.6(3) |
| CoO(1)C(1) | 113.8(4) | CoO(1')C(1') | 114.8(4) |
| O(1)C(1)O(2) | 120.4(6) | O(1')C(1')O(2') | 122.5(6) |
| O(1)C(1)C(2) | 118.5(6) | O(1')C(1')C(2') | 117.7(6) |
| C(1)C(2)N(1) | 108.4(5) | C(1')C(2')N(1') | 106.0(6) |
| CoN(1)C(2) | 108.6(5) | CoN(1')C(2') | 106.4(4) |
| N(1)C(2)C(3) | 112.0(6) | N(1')C(2')C(3') | 114.8(6) |
| C(1)C(2)C(3) | 113.0(7) | C(1')C(2')C(3') | 112.0(7) |
| C(2)C(3)C(4) | 110.0(6) | C(2')C(3')C(4') | 113.2(7) |
| C(3)C(4)C(5) | 111.9(7) | C(3')C(4')C(5') | 108.0(7) |
| C(4)C(5)N(2) | 105.7(6) | C(4')C(5')N(2') | 111.7(7) |
| C(5)N(2)C(6) | 123.2(6) | C(5')N(2')C(6') | 122.8(7) |
| N(2)C(6)N(3) | 119.3(6) | N(2')C(6')N(3') | 119.6(6) |
| N(2)C(6)N(4) | 120.5(7) | N(2')C(6')N(4') | 121.6(6) |
| N(3)C(6)N(4) | 120.1(6) | N(3')C(6')N(4') | 118.8(7) |
| CoN(6)O(6) | 118.7(5) | CoN(6')O(6') | 120.4(6) |
| CoN(6)O(7) | 121.2(5) | CoN(6')O(7') | 115.6(6) |
| O(6)N(6)O(7) | 120.1(7) | O(6')N(6')O(7') | 124.0(7) |
| O(3)N(5)O(4) | 120.1(7) | O(4)N(5)O(5) | 119.8(7) |
| O(3)N(5)O(5) | 120.2(6) | | |

**Table IV.** Summary of the torsion angles in Cobalt(L-arginine) and other reported arginine compounds.

| Internal Rotation Angles | Unprimed Ligand | Primed Ligand | Arg.$H_3PO_4$ . $H_2O$ | Arg.$2H_2O$ | Arg.HCl | | Arg.HCl . $H_2O$ | | Arg.HBr . $H_2O$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Mol 1 | Mol 2 | Mol 1 | Mol 2 | Mol 1 | Mol 2 |
| (1) = O(1)C(1)C(2)N(1) | 9 | 27 | —34 | —11 | —51 | —41 | —6 | —26 | —6 | —29 |
| O(1)C(1)C(2)C(3) | 133 | 153 | 84 | 111 | 71 | 79 | 116 | 97 | 115 | 95 |
| (2) = O(2)C(1)C(2)N(1) | —172 | —156 | 148 | 168 | 135 | 138 | 178 | 157 | 177 | 156 |
| O(2)C(1)C(2)C(3) | —47 | —30 | —94 | —70 | —104 | —102 | —60 | —80 | —61 | —80 |
| (1) = N(1)C(2)C(3)C(4) | 77 | —70 | —164 | 62 | 171 | 168 | —63 | —54 | —61 | —55 |
| C(1)C(2)C(3)C(4) | —47 | 170 | 78 | —60 | 49 | 49 | 178 | —175 | 178 | —177 |
| (2) = C(2)C(3)C(4)C(5) | —167 | —172 | 175 | 151 | —173 | 166 | —166 | 172 | —163 | 168 |
| (3) = C(3)C(4)C(5)N(2) | —173 | —176 | —64 | 175 | 172 | 175 | —179 | —175 | —180 | —174 |
| (4) = C(4)C(5)N(2)C(6) | —173 | —170 | 113 | 162 | —172 | 170 | —81 | 100 | —86 | 101 |
| (5) = C(5)N(2)C(6)N(3) | 176 | —179 | —176 | 172 | 175 | —179 | —169 | 165 | —167 | 165 |
| (6) = C(5)N(2)C(6)N(4) | 0 | 0 | 5 | —8 | —7 | 6 | 13 | —19 | 9 | —18 |

amino nitrogens N(1) and N(1′) and the carboxylate oxygens O(1) and O(1′). The guanidyl groups of the amino acids do not coordinate to the cobalt. Bond distances and bond angles are given in Table III along with several intermolecular distances which influence the packing in the unit cell. Torsion angles for the arginine ligands in this structure and in other reported structures are given in Table IV. The sense of rotation of the torsion angles is consistent with the rules proposed by Edsall, *et al.*[18] and Klyne and Prelog.[19] Table V gives the least-squares equations for planes passed through significant structural groups and the distance of each atom from the plane.

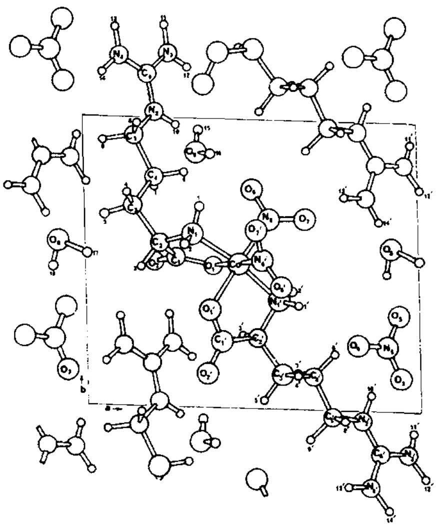

Figure 1. Projection of the unit cell contents onto the ab plane for (+)-dinitrobis-(L-arginato)cobalt(III) nitrate dihydrate.

The coordination geometry about the cobalt is that of a distorted octahedron with the two nitro groups in a *cis* configuration. Celap, *et al.*[18] have shown that the nitro groups are in the *cis* configuration for a series of dinitrobis-(amino acidato)cobalt(III) ions. The distortions of the angles about the cobalt ion are associated primarily with the restrictions imposed by the five-membered chelate rings, O(1)–Co–N(1)=85.8° and O(1′)–Co–N(1′)=84.7°. These angles are consistent with those observed for other amino acid complexes. The average of seventeen O–$Cu^{II}$–N

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(18) J. T. Edsall, P. T. Flory, J. C. Kendrew, A. M. Liquori, G. Nemethy, G. N. Ramachandran, and H. A. Scheraga, *J. Molec. Biol.*, *15*, 399 (1966).

(19) W. Klyne and V. Prelog, *Experientia*, *16*, 521 (1960).

angles in five-membered chelate rings involving amino acids is 83.5°.[1]

The absolute configuration about the cobalt ion is R—[20] which is equivalent to the P($C_2$) notation pro-

**Table V.** Least-squares equations for groups of atoms and the deviations of the atoms from each plane. The equation of each plane is defined by Ax+By+Cz = D where y is parallel to *b*, x is parallel to the projection of *a* on a plane perpendicular to *b* and z is perpendicular to x and y[b]

(1) Chelate Ring Plane

| | Unprimed Ligand | Primed Ligand |
|---|---|---|
| O(1) | —0.009 | —0.087 |
| O(2) | 0.049 | 0.130 |
| C(1) | —0.013 | —0.030 |
| C(2) | —0.072 | —0.229 |
| N(1) | 0.063 | 0.203 |
| Co | —0.376 | —0.256 |
| A | 0.209 | 0.545 |
| B | 0.923 | —0.175 |
| C | —0.324 | 0.820 |
| D | 4.831 | 4.557 |

(2) Carboxylate Group Plane

| | Unprimed Ligand | Primed Ligand |
|---|---|---|
| O(1) | 0.000 | —0.005 |
| O(2) | 0.000 | —0.005 |
| C(1) | 0.000 | 0.013 |
| C(2) | 0.000 | —0.004 |
| N(1)[a] | 0.202 | 0.609 |
| Co[a] | —0.251 | 0.112 |
| A | 0.276 | 0.645 |
| B | 0.934 | —0.075 |
| C | —0.276 | 0.761 |
| D | 4.980 | 4.999 |

(3) Guanidyl Group Plane

| | Unprimed Ligand | Primed Ligand |
|---|---|---|
| N(2) | 0.005 | 0.001 |
| C(6) | —0.014 | —0.004 |
| N(3) | 0.005 | 0.001 |
| N(4) | 0.005 | 0.001 |
| A | 0.678 | 0.702 |
| B | 0.204 | 0.168 |
| C | 0.706 | 0.692 |
| D | 3.193 | 6.219 |

(4) Carbon Side Chain Plane

| | Unprimed Ligand | Primed Ligand |
|---|---|---|
| C(2) | 0.069 | —0.045 |
| C(3) | —0.091 | 0.055 |
| C(4) | —0.059 | 0.033 |
| C(5) | 0.094 | —0.051 |
| N(2)[a] | —0.017 | 0.007 |
| A | 0.529 | 0.701 |
| B | 0.348 | 0.403 |
| C | 0.774 | 0.588 |
| D | 5.044 | 6.034 |

(5) Nitrate Group Plane

| | |
|---|---|
| N(5) | 0.001 |
| O(3) | 0.000 |
| O(4) | 0.000 |
| O(5) | 0.000 |
| A | 0.650 |
| B | 0.075 |
| C | 0.756 |
| D | 9.155 |

[a] These atoms were not included in the least-squares plane calculation. [b] The transformation from the triclinic cell (X,Y,Z) to the orthogonal cell is given by

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 11.232 & 0 & -.907 \\ -.631 & 9.867 & .051 \\ 0 & 0 & 5.628 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

**Table VI.** Intermolecular distances involving hydrogen atoms.

| Donor (D) | Acceptor (A) | Distance (D) . . . (A) | Distance H . . . (A) | Angle (D)-H . . . (A) |
|---|---|---|---|---|
| N(1) | O(W) | 3.112(Å) | 2.27(Å) | 142° |
| O'(W) | O(5) | 2.848 | 1.88 | 161° |
| O(W) | O'(2) | 2.785 | 1.88 | 176° |
| O(W) | O(6) | 3.234 | 2.14 | 149° |
| N(2) | O(W) | 3.054 | 2.04 | 165° |
| N'(3) | O'(W) | 2.935 | 2.07 | 145° |
| N'(4) | O'(W) | 2.887 | 2.00 | 148° |
| O'(W) | O(2) | 2.794 | 2.10 | 133° |
| N(3) | O(2) | 2.934 | 2.04 | 149° |
| N(4) | O(2) | 3.124 | 2.31 | 139° |
| N'(4) | O(7) | 3.074 | 2.13 | 157° |
| N(4) | O(3) | 2.899 | 1.96 | 157° |
| N(4) | O(5) | 2.976 | 2.67 | 98° |
| N'(3) | O(3) | 2.914 | 1.93 | 169° |
| N'(2) | O(4) | 2.954 | 1.92 | 153° |
| N(3) | O'(1) | 2.926 | 2.65 | 117° |
| N(3) | O'(2) | 2.978 | 2.01 | 165° |

posed by McCaffery, *et al.*[21] for designating the absolute configuration of bisdiamine complexes. This study confirms the assignment made from circular dichroism studies.[8]

The cobalt(III)-oxygen bond lengths of 1.909 and 1.911 Å may be compared with the value of 1.91 Å found in (–)–sarcosinatobis(ethylene-diamine)cobalt-(III) diiodide dihydrate[22] and 1.85 Å reported for a bis-glycylglycinate-cobalt(III) complex.[10] The $Co^{III}$-nitrogen bond lengths of 1.935, 1.977, 1.894 and 1.941 Å may be compared with the values of 1.97 Å and 1.92 Å reported for the above two complexes.

Least-squares planes fitted to the five-membered chelate rings of the arginine ligands indicate the rings are not planar. Planes fitted to the carboxylate groups and the adjqacent carbon atoms show N(1) to be 0.20 Å out of the plane while N(1′) is 0.61 Å from the plane. The torsion angle about C(1)–C(2) is +9° while that about C(1′)–C(2′) is +27°. These torsion angles are consistent with the magnitudes observed for several α-amino acids, but they are of opposite signs.

Least-squares planes fitted to the guanidyl groups indicate they are planar within experimental error and normals to the carboxylate planes and the guanidyl planes of the two ligands make angles of 82° and 15°, respectively. The conformations of the two arginine ligands are indicated by the torsion angles given in Table IV. One of the major differences between the two ligands is the torsion angle N(1)–C(2)–C(3)–C(4). In the unprimed ligand this angle is 77° leaving C(4) staggered betweeen the $NH_2$ and COO groups. This is not the sterically favored orientation, but has been observed in the L-arginine dihydrate structure.[2] The torsion angle for the primed ligand is –70° which leaves C(4′) staggered between the $NH_2$ group and a hydrogen on C(2′). Packing interactions appear to be responsible for the orientation of the side chains.

The bond lengths and angles for each of the arginine ligands are consistent with those reported for other arginine structures.[7] The average carbon-carbon distance is 1.54 Å and the average C-N distance is 1.33 Å. The C-N distances indicate some delocalization in the protonated guanidyl groups.

The N-O distances in the nitro groups average 1.22 Å while the N-O distances in the nitrate group average 1.23 Å. The bond angles are consistent with $sp^2$ hybridization. The cobalt(III) ion lies in the plane of each nitro group. The nitrate group is planar.

Table VI lists distances between potential hydrogen bonded atoms. Contact distances between nitrogen and oxygen atoms of 2.75 to 3.15 Å have been associated with hydrogen bonding in many cases.[23] The oxygen atoms of the water molecules act as both acceptors and donors in the formation of hydrogen bonds while the guanidyl groups probably are involved as hydrogen bond donors. The carboxylate oxygen atoms of both ligands are involved as hydrogen bond acceptors as probably are oxygens O(7) and O(5) of the nitro and nitrate groups. Each group in the structure appears to assume an orientation in the unit cell which permits the most extensive hydrogen bonding network.

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