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# Binding of Penicillamine to Toxic Metal Ions: Synthesis and Structure of Potassium (D-Penicillaminato)(L-penicillaminato)cobaltate(III) Dihydrate, K[Co(D-pen)(L-pen)]·$2H_2O$

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**Abstract:** The complex potassium (D-penicillaminato)(L-penicillaminato)cobaltate(III) dihydrate, K[Co(D-pen)(L-pen)]·$2H_2O$, $C_{10}H_{22}CoKN_2O_6S_2$, has been synthesized and its crystal structure has been determined from three-dimensional single-crystal x-ray counter data. The complex crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a$ = 10.667 (4) Å, $b$ = 15.413 (7) Å, $c$ = 5.721 (3) Å, $\alpha$ = 106.64 (3)°, $\beta$ = 100.74 (3)°, and $\gamma$ = 64.88 (2)°. Full-matrix least-squares refinement of the structure has converged to a $R$ factor (on $F$) of 0.038 for 2901 independent intensities. The geometry about the cobalt(III) centers is roughly octahedral, the ligating atoms being the S, N, and O atoms of the two penicillamine dianions. The isomer isolated is the all-cis isomer. The two Co–S bond lengths of 2.222 (2) and 2.229 (1) Å are similar to each other and to those in related complexes, but the Co–N distances of 1.922 (3) and 1.983 (3) Å and the Co–O lengths of 1.971 (2) and 1.942 (2) Å show a wide variation.

The increase in the industrial[1] and agricultural[2] use of metal and organometallic complexes of the last 2 decades has been accompanied by an increasing number of outbreaks of metal poisoning.[1-3] It is well established that toxic metal ions can, in some cases, be removed from the living system by the administration of chelating agents, which preferentially bind to the metal ions and, thereby, release them from the macromolecules (notably proteins) to which they coordinate. Many of the more successful chelating agents contain soft donors; thus, for example, dimercaptosuccinic acid,[4] BAL (2,3-dimercaptopropanol), and D-penicillamine ($\beta,\beta$-dimethyl-D-cysteine) contain sulfur atoms, and recent research[5] has suggested that selenium donors may be equally effective. Of the sulfur-containing chelating agents, D-penicillamine is the simplest to use since (unlike BAL), it is not toxic and can be administered in aqueous solution.

While the majority of chemical and clinical research has centered on the metals lead,[6] mercury,[7] and copper,[8] other metals are now commonly found in the environment; specifically, cobalt is in widespread industrial use[9] in catalytic processes, high-fidelity equipment, and pigments. The toxic effects of cobalt poisoning include heart disease and excess formation of red corpuscles; in the last decade, at least 40 people are known to have died from heart disease as a direct result of cobalt poisoning.[10] We have, therefore, initiated a study of the chelation of cobalt ions by therapeutic ligands.

The simplest complexes of transition metal ions with the potentially tridentate ligands cysteine, penicillamine, methionine, and their derivatives which would be anticipated are the *pseudo*-octahedral $ML_2$ species; there is, however, no firm structural evidence for the existence of octahedral complexes $M(pen)_2$, although recent work in our laboratories has established that this mode of binding does occur[11] for *S*-methyl-L-cysteine (SMC) anion in $[Co(SMc)_2]^+$ and for L-cysteine dianion (L-cys) in[12] $[Cr(\text{L-cys})_2]^-$.

We have, therefore, examined the reaction of cobalt(II) salts with penicillamine, and here report the synthesis and crystal structure of the complex potassium (D-penicillaminato)(L-penicillaminato)cobaltate(III) dihydrate, K[Co(D-pen)(L-pen)]·$2H_2O$.

## Experimental Section

**Synthesis.** Cobalt(II) nitrate (0.005 mol in 7 mL of water) was added to D,L-penicillamine (0.015 mol in 20 mL of water) and the resulting mixture was stirred for a few minutes. Potassium hydroxide was added until the pH of the solution reached approximately 7. The solution was filtered and the filtrate allowed to stand; large olive green needles precipitated after several days. The crystals decompose slowly in air, with apparent loss of water, but their approximate composition was determined by chemical analysis and shown to be consistent with their formulation as a hydrate of K[Co(D-pen)(L-pen)]. The crystallographic experiments (vide infra) demonstrate that the original crystals are the dihydrate. Anal. Calcd for $C_{10}H_{22}CoKN_2O_6S_2$: C, 28.03; H, 5.18; N, 6.54; K, 9.13; S, 14.97. Obsd: C, 30.98; H, 5.03; N, 6.81; K, 9.86; S, 15.29.

**Collection and Reduction of the X-ray Data.** On the basis of Weissenberg and procession photography, the crystals were assigned to the triclinic system; the space group was initially selected as the centrosymmetric choice $P\bar{1}$ ($C_i^1$), and this was confirmed by the successful refinement of the structure (vide infra). The cell constants, obtained by least-squares methods,[13] are $a$ = 10.667 (4) Å, $b$ = 15.413 (7) Å, $c$ = 5.721 (3) Å, $\alpha$ = 106.64 (3)°, $\beta$ = 100.74 (3)°, and $\gamma$ = 64.88 (2)°. The observations were made at 21° with the wavelength assumed as $\lambda$(Mo K$\alpha_1$) 0.7093 Å. A density of 1.749 g cm$^{-3}$ calculated for two molecules per cell is in acceptable agreement with the value of 1.76 (3) g cm$^{-3}$ observed by flotation. Hence, in space group $P\bar{1}$, no crystallographic symmetry is imposed on the molecules.

Intensity data were gathered from a prismatic crystal bounded by the (010), (0$\bar{1}$0), (210), ($\bar{2}\bar{1}$0), (00$\bar{1}$), and (001) faces. The distances between these opposite pairs of faces were approximately 0.008, 0.016, and 0.064 cm, respectively. The crystal was mounted on a fiber roughly parallel to the $a$ axis. The data were collected at a takeoff angle of 1.6°, with a receiving aperture 5.0 × 5.0 mm, placed 32 cm from the crystal. The data were collected by the $\theta/2\theta$ scan technique, the scans being from 0.9° below the calculated K$\alpha_1$ peak position to 0.9° above the

**Table I.** Positional Parameters (× 10$^4$) for Nonhydrogen Atoms in K[Co(D-pen)(L-pen)]·2$H_2O$

| Atom | *X* | *Y* | *Z* |
|---|---|---|---|
| Co | 0.887.0 (4) | 2337.1 (3) | 0737.3 (8) |
| K | 2809.5 (8) | 0060.6 (6) | 2837 (2) |
| Sa | −0897.4 (9) | 3607.2 (7) | 2547 (2) |
| Sb | 2206.8 (9) | 2368.6 (7) | 4248 (1) |
| O1a | 0161 (2) | 1460 (2) | 1310 (5) |
| O2a | −1796 (3) | 1205 (2) | 0523 (5) |
| O1b | 2453 (2) | 1217 (2) | −0928 (4) |
| O2b | 4583 (2) | 0876 (2) | −1805 (5) |
| Na | −0345 (3) | 2263 (3) | −2308 (6) |
| Nb | 1757 (3) | 3090 (2) | 0034 (6) |
| C1a | −1059 (4) | 1602 (3) | 0280 (7) |
| C2a | −1591 (3) | 2352 (3) | −1332 (7) |
| C3a | −2270 (3) | 3409 (3) | 0242 (7) |
| C4a | −3472 (4) | 3515 (4) | 1538 (9) |
| C5a | −2813 (5) | 4162 (4) | −1325 (9) |
| C1b | 3493 (3) | 1439 (3) | −0886 (6) |
| C2b | 3263 (3) | 2499 (2) | 0488 (6) |
| C3b | 3575 (3) | 2596 (3) | 3268 (6) |
| C4b | 3483 (5) | 3639 (3) | 4569 (8) |
| C5b | 5012 (4) | 1846 (3) | 3846 (8) |
| OW1 | 1602 (7) | −0231 (4) | −3860 (11) |
| OW2[a] | −0052 (9) | 4814 (5) | −2135 (15) |
| OW3[a] | −0837 (12) | 0165 (13) | 4645 (23) |

[a] The occupancy factors of these disordered positions were assigned as 0.5.

**Table III.** Selected Interatomic Separations in K[Co(D-pen)(L-pen)]·2$H_2O$

| Atoms | *D* (Å) | Atoms | *D* (Å) |
|---|---|---|---|
| Co-SA | 2.222 (2) | Co-SB | 2.229 (1) |
| Co-NA | 1.983 (3) | Co-NB | 1.922 (3) |
| Co-O1A | 1.942 (2) | Co-O1B | 1.971 (2) |
| C1A-O1A | 1.279 (4) | C1B-O1B | 1.287 (4) |
| C1A-O2A | 1.230 (4) | C1B-O2B | 1.221 (4) |
| C1A-C2A | 1.539 (5) | C1B-C2B | 1.531 (5) |
| C2A-NA | 1.475 (4) | C2B-NB | 1.488 (4) |
| C2A-C3A | 1.547 (5) | C2B-C3B | 1.540 (5) |
| C3A-SA | 1.845 (4) | C3B-SB | 1.850 (3) |
| C3A-C4A | 1.526 (5) | C3B-C4B | 1.534 (5) |
| C3A-C5A | 1.522 (6) | C3B-C5B | 1.524 (5) |
| C2A-HCA2 | 1.07 (4) | C2B-HCB2 | 0.91 (4) |
| C4A-H4A1 | 0.95 (5) | C4B-H4B1 | 0.97 (4) |
| C4A-H4A2 | 1.00 (5) | C4B-H4B2 | 0.94 (5) |
| C4A-H4A3 | 0.95 (6) | C4B-H4B3 | 0.93 (4) |
| C5A-H5A1 | 1.00 (4) | C5B-H5B1 | 0.95 (4) |
| C5A-H5A2 | 1.07 (5) | C5B-H5B2 | 0.90 (4) |
| C5A-H5A3 | 0.89 (5) | C5B-H5B3 | 0.94 (5) |
| NA-HNA1 | 0.92 (4) | NB-HNB1 | 0.87 (4) |
| NA-HNA2 | 0.79 (4) | NB-HNB2 | 0.84 (5) |

calculated K$\alpha_2$ peak position. The scan rate was 2.0 deg/min in 2$\theta$, and backgrounds were collected for 10 s at each end of the scans.

A unique data set having 2$\theta$(Mo) ≤ 54° was collected; a total of 3870 intensities was recorded. There were very few observable intensities at 2$\theta$ values higher than 54°. The intensities of three standard reflections were recorded periodically throughout the run, and exhibited no decline as a function of cumulative exposure time. Of the 3870 intensities, 2901 were greater than three times their estimated standard deviations; only these reflections were used in the refinement of the structure.

The data were processed in the manner described by Ibers and coworkers;[14] the values of $I$ and $\sigma(I)$ were corrected for Lorentz-polarization and for absorption effects. The absorption coefficient for these atoms with Mo K$\alpha$ radiation is 16.4 cm$^{-1}$, and for the sample chosen the transmission coefficients[15] were in the range 0.78–0.91.

**Solution and Refinement of the Structure.** The positions of the cobalt atom and one sulfur atom were determined from a three-dimensional Patterson function, and were refined by least-squares techniques. Least-squares refinements were on $F$, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ where the weights, $w$, were $4F_o^2/\sigma^2(F_o^2)$. In computations of $F_c$, the scattering factors for hydrogen were from Stewart, Davidson, and Simpson,[16] and those for other atoms were from International Tables.[17a] The effects of the anomalous dispersion of cobalt, sulfur, and potassium were included in the values of $F_c$,[18] the values of $\Delta f'$ and $\Delta f''$ being taken from International Tables.[17b] After two cycles of least-squares refinement of the cobalt and one sulfur position, the conventional agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ were 0.510 and 0.558, respectively. The remaining nonhydrogen atoms, with the exception of the water oxygen atoms, were readily located in subsequent difference Fourier maps. One of the water molecules is clearly disordered, occupying two positions each of which is quite close to an

**Table II.** Thermal Parameters for Nonhydrogen Atoms (× 10$^4$, except for Co, K, and S, which are × 10$^5$)

| Atom | $\beta_{11}$[a] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Co | 455 (5) | 309 (3) | 977 (14) | −147 (3) | 140 (6) | 139 (4) |
| K | 607 (9) | 394 (5) | 5823 (53) | −149 (5) | 129 (17) | 432 (13) |
| SA | 530 (9) | 421 (5) | 1763 (30) | −143 (5) | 234 (13) | −31 (10) |
| SB | 565 (9) | 494 (5) | 987 (25) | −237 (6) | 73 (12) | 268 (9) |
| O1A | 63 (2) | 38 (1) | 222 (9) | −22 (2) | 16 (4) | 31 (3) |
| O2A | 102 (3) | 62 (2) | 324 (12) | −54 (2) | 11 (5) | 40 (4) |
| O1B | 57 (2) | 30 (1) | 183 (8) | −13 (1) | 34 (4) | 7 (3) |
| O2B | 62 (3) | 42 (1) | 252 (10) | −7 (2) | 58 (4) | 16 (3) |
| NA | 66 (3) | 44 (2) | 124 (10) | −22 (2) | 20 (5) | 16 (4) |
| NB | 53 (3) | 32 (2) | 102 (9) | −10 (2) | 12 (4) | 20 (3) |
| C1A | 71 (4) | 42 (2) | 174 (12) | −28 (2) | 29 (6) | 4 (4) |
| C2A | 58 (3) | 48 (2) | 160 (12) | −30 (2) | −2 (5) | 17 (4) |
| C3A | 50 (3) | 50 (2) | 178 (12) | −17 (2) | 10 (5) | 27 (4) |
| C4A | 52 (4) | 67 (3) | 275 (16) | −20 (3) | 37 (7) | 20 (6) |
| C5A | 94 (5) | 62 (3) | 297 (18) | −15 (3) | 4 (8) | 69 (6) |
| C1B | 54 (3) | 40 (2) | 108 (10) | −13 (2) | 15 (5) | 26 (4) |
| C2B | 46 (3) | 35 (2) | 138 (11) | −16 (2) | 20 (5) | 26 (4) |
| C3B | 54 (3) | 43 (2) | 122 (10) | −23 (2) | 9 (5) | 17 (4) |
| C4B | 98 (5) | 50 (3) | 193 (14) | −41 (3) | 9 (7) | 2 (5) |
| C5B | 57 (4) | 60 (3) | 214 (14) | −23 (3) | −8 (6) | 54 (5) |
| OW1 | 340 (13) | 93 (4) | 562 (29) | −64 (6) | 145 (15) | 20 (8) |
| OW2 | 198 (11) | 69 (5) | 480 (35) | −36 (6) | 43 (17) | 56 (11) |
| OW3 | 213 (18) | 242 (15) | 563 (52) | −153 (14) | 140 (23) | 236 (23) |

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Bond Angles (deg) in the [Co(D-pen)(L-pen)]$^-$ Anion

| | | | |
|---|---|---|---|
| NB-Co-O1A | 174.3 (1) | O2A-C1A-C2A | 120.4 (3) |
| NB-Co-O1B | 82.7 (1) | O1B-C1B-O2B | 125.0 (3) |
| NB-Co-Na | 98.7 (1) | O1B-C1B-C2B | 113.6 (3) |
| NB-Co-SA | 97.0 (1) | O2B-C1B-C2B | 121.4 (3) |
| NB-Co-SB | 85.1 (1) | C1A-C2A-C3A | 110.1 (3) |
| O1A-Co-O1B | 91.6 (1) | C1A-C2A-NA | 105.5 (3) |
| O1A-Co-NA | 81.7 (1) | C3A-C2A-NA | 108.7 (3) |
| O1A-Co-SA | 88.70 (8) | C1B-C2B-C3B | 111.8 (3) |
| O1A-Co-SB | 94.57 (8) | C1B-C2B-NB | 105.5 (3) |
| O1B-Co-NA | 90.6 (1) | C3B-C2B-NB | 107.7 (3) |
| O1B-Co-SA | 178.9 (1) | SA-C3A-C2A | 105.9 (2) |
| O1B-Co-SB | 90.16 (8) | SA-C3A-C4A | 109.3 (3) |
| NA-Co-SA | 88.4 (1) | SA-C3A-C5A | 110.9 (3) |
| NA-Co-SB | 176.2 (1) | C2A-C3A-C4A | 111.2 (3) |
| SA-Co-SB | 90.85 (6) | C2A-C3A-C5A | 110.9 (3) |
| Co-SA-C3A | 97.0 (1) | C4A-C3A-C5A | 108.7 (3) |
| Co-SB-C3B | 98.3 (1) | SB-C3B-C2B | 105.2 (2) |
| Co-O1A-C1A | 112.2 (2) | SB-C3B-C4B | 109.6 (3) |
| Co-O1B-CB | 112.3 (2) | SB-C3B-C5B | 111.0 (3) |
| Co-NA-C2A | 100.6 (2) | C2B-C3B-C4B | 110.6 (3) |
| Co-NB-C2B | 103.1 (2) | C2B-C3B-C5B | 110.9 (3) |
| O1A-C1A-O2A | 125.3 (4) | C4B-C3B-C5B | 109.5 (3) |
| O1A-C1A-C2A | 114.3 (3) | | |

inversion center; the two disordered positions were assigned occupancy factors of 0.5, and the positions and thermal parameters of each "half oxygen" atom were refined separately. The hydrogen atoms associated with the penicillaminato ligands were all found in a difference Fourier map, but those on the water molecules could not be located. A least-squares calculation in which all nonhydrogen atoms were refined anisotropically and the ligand hydrogen atoms were refined isotropically converged to values of $R_1$ and $R_2$ of 0.038 and 0.047, respectively. Attempts to refine the structure in the noncentrosymmetric space group $P1$ were unsuccessful, which indicates that our choice of $P\bar{1}$ is correct.

The final cycle of least-squares refinement involved 2901 reflections and 280 variables, for a reflection:variable ratio of approximately 10.4:1. Examination of the values of $|F_o|$ and $|F_c|$ suggested to us that no correction for secondary extinction was necessary. In the final cycle of refinement, no parameter experienced a shift of more than 0.34$\sigma$, which is taken as evidence for convergence. A final difference Fourier map showed some peaks of approximately 0.7 e Å$^{-3}$ in the vicinity of the cobalt atoms but was otherwise featureless. The value of $R_2$ showed no unusual dependence on either sin $\theta$ or $|F_c|$.

The positional and thermal parameters of the nonhydrogen atoms are listed in Tables I and II, along with their standard deviations as estimated from the inverse matrix. The positional and thermal parameters of the hydrogen atoms, and a listing of observed and calculated structure amplitudes, are available.[19]

## Description of the Structure

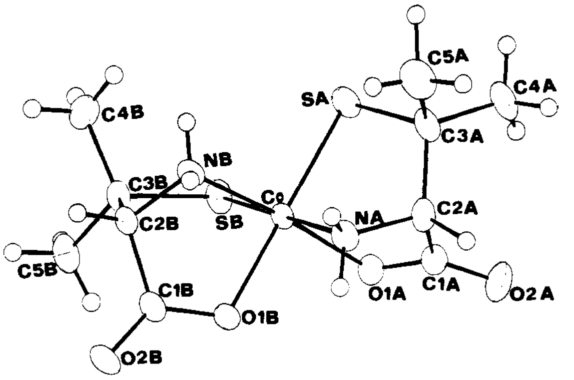

Figure 1. View of the [Co(D-pen)(L-pen)]$^-$ ion in K[Co(D-pen)(L-pen)]·$2H_2O$. The L-pen ring is on the left in this view. Thermal ellipsoids are drawn at the 40% probability level, but hydrogen atoms are shown as unlabeled spheres of arbitrary size.

The structure consists of discrete [Co(D-pen)(L-pen)]$^-$ anions which interact with the potassium cations and the water molecules. The structure of the anion is shown in Figure 1. The coordination geometry about the cobalt(III) center is roughly octahedral, and ligating atoms being S, N, and one O atom from each of two penicillaminato dianions. The isomer which precipitated is the all-cis isomer. The bond lengths and angles in the anion are listed in Tables III and IV. The Co-S bond lengths of 2.222 (2) and 2.229 (1) Å are very similar to the value[20,21] of 2.228 (1) Å in [Co(L-his)(D-pen)], and are significantly shorter (and, presumably, stronger) than the bond of 2.272 (2) Å in the *S*-methyl-L-cysteinato complex[11] [Co(SMC)$_2$]$^+$. In pen ring B (shown as the L-pen ring in Figure 1), the Co-N distance of 1.922 (3) Å is much shorter than the values of 1.946 (6) and 1.973 (8) Å in the SMC and (L-his)(D-pen) complexes, respectively, while the Co-O bond length of 1.971 (2) Å is longer than the values of 1.906 (5) and 1.921 (3) Å, respectively, in these two complexes.[11,20,21] In ring A, however, both the Co-N and Co-O bonds of 1.983 (3) and 1.942 (2) Å, respectively, are longer than the analogous bonds in these other complexes. Hence, on the basis of bond length data above, it would appear that the ligand binding in the present complex may be weaker than that in the other complexes; stability constant data are not yet available for any of these complexes to our knowledge. The chelating bond angles involving ring A are SA-Co-NA = 88.4 (1)°, SA-Co-O(1)A = 88.70 (8)°, and Na-Co-O(1)A = 81.7 (1)°, and those for ring B are SB-Co-NB = 85.1 (1)°, SB-Co-O(1)B = 90.16 (8)°, and NB-Co-O(1)B = 82.7 (1)°. In each case, as expected, the largest angle is associated with the largest (six-membered) ring. The geometry of the pen$^{2-}$ anions is normal, the bond lengths in the A ring being substantially similar to those in the B ring. The dihedral angles associated with the ligands are compared with those in other complexes in Table V.

The environment of the potassium cations is extremely irregular. There appear to be Coulombic interactions between the potassium ion and the terminal carboxyl oxygen atoms O2(A) and O2(B), and also with sulfur atom SB and water oxygen atom W(1); the distances associated with these interactions of 2.745 (3), 2.624 (3), 3.213 (2), and 2.705 (7) Å, respectively, are all similar to the sums of the ionic radius of

Table V. Dihedral Angles (degrees) in [Co(D-pen)(L-pen)]$^-$ and Related Complexes

| Atoms | [Co(D-pen)(L-pen)]$^-$ Ring A (D) | Ring B (L) | [Co(D-pen)(L-his)] | [Co(L-SMc)$_2$]$^+$ Ligand I | Ligand II |
|---|---|---|---|---|---|
| O1-C1-C2-C3 | −85.7 | 82.9 | −81.0 | 78.9 | 83.8 |
| O1-C1-C2-N | 31.4 | −33.7 | 35.8 | −34.6 | −32.5 |
| N-C2-C3-S | −55.1 | 47.8 | −44.4 | 44.7 | 49.2 |
| Co-N-C2-C3 | 68.8 | −70.8 | 68.8 | −69.7 | −70.9 |
| Co-N-C2-C1 | −49.3 | 48.6 | −49.1 | 45.0 | 47.2 |
| Co-O1-C1-C2 | 5.3 | 1.5 | −2.0 | — | — |
| Co-S-C3-C2 | 15.1 | −8.1 | 2.8 | −3.7 | −8.6 |
| Reference | This work | | 21 | 11 | |

**Table VI.** Probable A-H···B Hydrogen Bonds

| A | H | B | H···B (Å) | A···B (Å) | A-H···B (deg) |
|---|---|---|---|---|---|
| NB | HNB1 | OW2 | 2.13 (4) | 2.965 (8) | 162 (3) |
| NB | HNB2 | SB | 2.47 (5) | 3.233 (4) | 151 (4) |

$K^+$ (1.33 Å) and the van der Waals radius of O (1.40 Å) or S (1.85 Å).[22] There are no other potassium-oxygen distances of less than 2.89 Å or potassium-sulfur distances less than 3.5 Å.

Hydrogen bonding in the crystals does not appear to be extensive, which may in part account for the observed disorder in the water molecules. As is shown in Table VI, the nitrogen atom of ring B appears to participate[23] in weak hydrogen bonding to the disordered water molecule OW2, with an NB···OW2 separation of 2.965 (8) Å and an associated NB-HNB1···OW2 angle of 162 (3)°. The same nitrogen atom is also involved in an intermolecular hydrogen bond to the sulfur atom SB of an adjacent anion, with an NB···SB separation of 3.233 (4) Å and an NB-HNB2···SB angle of 151 (4)°. The amine group of ring A does not appear to engage in hydrogen bonding.

## Discussion

In the absence of solution thermodynamic data, it is not possible to determine whether the observed stereochemistry of the product is due to some thermodynamic stereochemical preference for the formation of $[\mathrm{Co(D\text{-}pen)(L\text{-}pen)}]^-$ relative to that of $[\mathrm{Co(D\text{-}pen)_2}]^-$ and $[\mathrm{Co(L\text{-}pen)_2}]^-$ or merely due to greater insolubility of the former. It is noteworthy in this context, that the analogous complex Co(D-pen)(L-his) is apparently less soluble in aqueous medium than Co(L-pen)(L-his).[21] In the 2:1 complexes of $\mathrm{pen}^{2-}$ with nickel(II) and zinc(II), however, a stereoselective effect in favor of the $[\mathrm{M(L\text{-}pen)_2}]^{2-}$ and $[\mathrm{M(D\text{-}pen)_2}]^{2-}$ over the meso form has been observed.[24] In the absence of crystallographic data for any nickel(II) or zinc(II) complex of penicillamine or cysteine, however, it is difficult to interpret this distinction in structural terms. The present complex represents the first structurally characterized $\mathrm{M(pen)_2}$ complex in which two pen ligands occupy the six sites of a metal's octahedral coordination sphere.

**Acknowledgment.** This research was supported by U.S. Public Health Service Grant No. ES00895-03 from the National Institute of Environmental Health Sciences.

**Supplementary Material Available:** A listing of observed and calculated amplitudes and positional and thermal parameters of hydrogen atoms (18 pages). Ordering information is available on any current masthead page.

## References and Notes

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