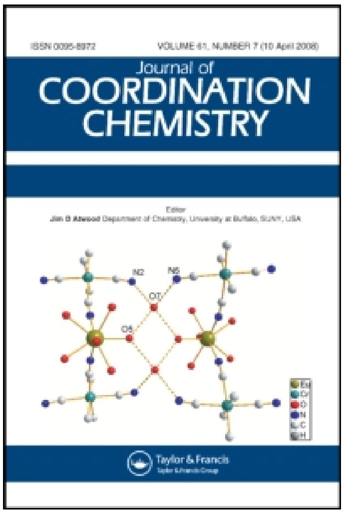

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# THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 43. THE CRYSTALLIZATION BEHAVIOR OF K[cis-α-Co(N-N'-$Et_2$-Edda)$(NO_2)_2$] · $2H_2O$ (I), {CS[cis-α-Co(Edda)$(NO_2)_2$]}$_2$ · $3H_2O$ (II), Rb[cis-α-Co(Edda)$(NO_2)_2$ · $H_2O$ (III) and $NH_4$[cis-α-Co(Edda)$(NO_2)_2$] · $2H_2O$ (IV)

Ivan Bernal[a]; Jiwen Cai[ab]; Fernando Somoza[ab]; William T. Jordan[c]; Karl M. Taft[c]
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# THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 43. THE CRYSTALLIZATION BEHAVIOR OF K[cis-α-Co(N-N'-$Et_2$-Edda)$(NO_2)_2$] · $2H_2O$ (I), {Cs[cis-α-Co(Edda)$(NO_2)_2$]}$_2$ · $3H_2O$ (II), Rb[cis-α-Co(Edda)$(NO_2)_2$ · $H_2O$ (III) and $NH_4$[cis-α-Co(Edda)$(NO_2)_2$] · $2H_2O$ (IV)

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K[*cis*-α-Co($Et_2$-edda)$(NO_2)_2$] · $2H_2O$ (I), $CoKO_{10}N_4C_{10}H_{22}$, crystallizes in the space group $P2_1/n$(No. 14), with lattice constants: $a = 7.339(2)$, $b = 15.750(3)$, $c = 15.492$ (4) Å and $\beta = 101.65(2)°$; $V = 1753.86$ Å$^3$ and $d$(calc; MW = 456.34, Z = 4) = 1.728 g-cm$^{-3}$. A total of 3335 data were collected over the range of $4° \leq 2\theta \leq 50°$; of these, 2553 (independent and with $I \geq 3\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 12.688$ cm$^{-1}$) and the transmission coefficients ranged from 0.8860 to 0.9997. Final values of the residuals were $R(F) = 0.0275$ and $R_w(F) = 0.0301$. The anions of the racemic pairs in the unit cell have the chiroptical symbols Λ(δλδ) and Δ(λδλ).

{Cs[*cis*-α-Co(edda)$(NO_2)_2$]}$_2$ · $3H_2O$ (**II**), $Cs_2Co_2O_{19}N_8C_8H_{18}$, crystallizes in the space group $C2/c$(No. 15), with lattice constants: $a = 19.304$ (6), $b = 10.992(4)$, $c = 13.809$ (5) Å and $\beta = 106.42(3)°$; $V = 2827.11$ Å$^3$ and $d$(calc; MW = 913.95 Z = 4) = 2.147 g-cm$^{-3}$. A total of 4192 data were collected over the range of $4° \leq 2\theta \leq 60°$; of these, 2837 (independent and with $I \geq 2.5\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 37.70$ cm$^{-1}$) and the transmission coefficients ranged from 0.2362 to 0.4458. Final values of the residuals were $R(F) = 0.034$ and $R_w(F) = 0.035$. The anions of the racemic pairs in the unit cell have the chiroptical symbols Δ(λδλ) and Λ(δλδ).

Rb[*cis*-α-Co(edda)$(NO_2)_2$] · $H_2O$ (**III**), $RbCoO_9N_4C_6H_{12}$, crystallizes in the space group $P\bar{1}$ (No. 2), with lattice constants: $a = 7.348$ (1), $b = 9.986(2)$, $c = 11.102$ (3) Å, $\alpha = 63.36(2)°$, $\beta = 66.23(2)°$ and $\gamma = 75.79(2)°$; $V = 664.27$ Å$^3$ and $d$(calc; MW = 428.58, Z = 2) = 2.143 g-cm$^{-3}$. A total of 2496 reflections were collected over the range of $4° \leq 2\theta \leq 60°$; of these, 1764 (independent and with $I \geq 2.5\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 48.80$ cm$^{-1}$) and the transmission coefficients ranged from 0.1891 to 0.3565. Final values of the residuals were $R(F) = 0.045$

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and $R_w$(F) = 0.052. The anions of the racemic pairs in the unit cell have the chiroptical symbols $\Delta(\lambda\delta\lambda)$ and $\Lambda(\delta\lambda\delta)$.

$NH_4$[*cis*-α-Co(edda)$(NO_2)_2$] · $2H_2O$ (**IV**), $CoO_{10}N_5C_6H_{18}$, crystallizes in the space group *C*2/*c*(No. 15), with lattice constants: $a = 23.240$ (14), $b = 7.101(9)$, $c = 20.948$ (17) Å and $\beta = 122.11(7)°$; $V = 2928.18$ Å$^3$ and *d*(calc; MW = 379.17, $Z = 8$) = 1.720 g-cm$^{-3}$. A total of 3474 data were collected over the range of $4° \leq 2\theta \leq 55°$; of these, 1639 (independent and with $I \geq 2.5\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 12.30$ cm$^{-1}$) and the transmission coefficients ranged from 0.6733 to 0.7570. Final values of the residuals were *R*(F) = 0.045 and $R_w$(F) = 0.049. The anions of the racemic pairs in the unit cell have the chiroptical symbols $\Lambda(\delta\lambda\delta)$ and $\Delta(\lambda\delta\lambda)$.

*Keywords:* chelate complex; cobalt (III); optical activity; crystal structure; cation effect

# INTRODUCTION

Hereafter, edda = N,N'-ethylediaminediacetato dianion, $Et_2$-edda = N,N'-diethyl-ethylendiaminediacetato dianion, edta = ethylendiaminetetracetato dianion.

Conglomerate crystallization is the phenomenon whereby a racemic solution produces a mechanical mixture of enantiomorphic crystals, the unit cell of which is homochiral.

Recently, we reported[1] on the crystallization behavior of K[*cis*-α-Co (edda)$(NO_2)_2$]·$nH_2O$ which was obtained in two different crystalline forms, $n = 0$(**V**) crystallizes as a conglomerate (space group $P2_12_12_1$) and $n = 1$(**VI**), crystallizes as a racemate (space group $P\bar{1}$). In both cases, we found infinite hydrogen-bonded strings running along the length of the crystals. In turn, the strings are linked to one another by O...K bonds and form a layer in which all strings are of the same chirality. And, whereas in (**V**) all the layers are of the same chirality, in crystals of (**VI**) individual layers are homochiral but adjacent layers are enantiomorphic to one another and related by the inversion centers of the space group $P\bar{1}$. In that report, we remarked on the propensity of conglomerate crystallization of edta and edda compounds and gave a list of those known to us to do so. We have found an additional one now,[2] namely aqua[ethylenediaminetriacetatoacetic acid]Co(III)·$3H_2O$.

In the earlier report,[1] we suggested that the following conditions were needed in order for these [*cis*-α-Co(edda)$(NO_2)_2$]$^-$ anions to crystallizes as conglomerates (a) the formation of hydrogen-bonded strings such as found in (**V**) must be possible and (b) the role of the charge compensating cation is also crucial, as witnessed by comparison of the crystallization pathway selected by (**V**) *vs.* (**VI**) in which the former has a bare $K^+$ cation whereas the latter has a $K(H_2O)^+$ cation to link the strings. Thus formation of strings was assumed to be a molecular, as opposed to a packing, phenomenon; the role of the water, in changing the coordination sphere around the linking $K^+$ ions, was suggested to be the cause of the modification in crystallographic behavior between (**V**) and (**VI**). In the case of (**I**), we tested suggestion (a) by alkylation of the ethylenediamine nitrogens since exchange of the N-H fragments for alkyl-N moieties was expected to destroy any chance of forming the required strings, should our proposal be correct. Likewise, we tested (b) by a change in charge compensating cation. Our findings are detailed below.

## EXPERIMENTAL

### Syntheses

K[*cis*-α-Co(Et$_2$-edda)(NO$_2$)$_2$] · 2H$_2$O **(I)** and K[*cis*-α-Co(edda)(NO$_2$)$_2$] **(V)** were prepared by the method of Jordan and Douglas.[3] Elemental analyses were already reported by those authors.

Compounds **(II)**, **(III)** and **(IV)** were obtained by passing solutions of **(V)** through packed columns of 100–200 mesh Dowex 50W-8 or 50W-X2 converted from the hydrogen form to the desired cation by passing a solution of the chloride or nitrate through the column until the pH of the eluted solution rose and stabilized. Crystalline product was obtained by evaporating the eluate in a stream of air at ambient temperature. The precipitate thus obtained was recrystallized from a minimum of hot deionized water. Crystals were filtered, washed with 95% ethanol and allowed to dry in air. Specimens suitable for crystallographic studies were found among them.

### Crystallography

Intensity data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[4] of the SDP-Plus software package.[5] For all four compounds, the procedure used for crystal alignment, cell constants and space group determination and data collection were uniform. They were centered with data in the $20° \leq 2\Theta \leq 40°$ range and examination of the cell constants, absences and Niggli matrix[6] showed them to crystallize in the space groups listed in Tables I through IV which summarize details of data collection and processing.

The intensity data were corrected for absorption using empirical curves derived from Psi scans[4,5] of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation.[7] During data collection, intensity and orientation standards were monitored and showed no significant deviations from the initial values. All data processing was done with the PC version of the NRCVAX program package.[8]

TABLE I Summary of data collection and processing parameters for racemic K[*cis*-α-Co $(Et_2edda)(NO_2)_2] \cdot 2H_2O$ (**I**)

| | |
|---|---|
| Space Group | $P2_1/n$(No. 14) |
| Cell Constants | $a$ = 7.339(2) Å |
| | $b$ = 15.750(3) |
| | $c$ = 15.492(4) |
| | β = 101.65(2)° |
| Cell Volume | $V$ = 1753.86 $Å^3$ |
| Molecular Formula | $KCoO_{10}N_4C_{10}H_{20}$ |
| Molecular Weight | 456.34 $gm\text{-}mole^{-1}$ |
| Density (calc; z = 4 mol/cell) | 1.728 $gm\text{-}cm^{-3}$ |
| Radiation Employed | $MoK_\alpha$ (λ = 0.71073 Å) |
| Absorption Coefficient | μ = 12.688 $cm^{-1}$ |
| Relative Transmission Coefficients | 0.8860 to 0.9997 |
| Data Collection Range | 4° ≤ 2Θ ≤ 50° |
| Scan Width | ΔΘ = 1.00 + 0.35tanΘ |
| Total Data Collected | 3206 |
| Data Used In Refinement* | 2553 |
| F(000) | 936 |
| $R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$ | 0.0275 |
| $Rw = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$ | 0.0301 |
| Weights Used | $w = [\sigma(F_o)]^{-2}$ |

* The difference between this number and the total is due to subtraction of 653 systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, were symmettry related, standards or did not meet the criterion that I ≥ 3σ(I).

TABLE II Summary of data collection and processing parameters for racemic {Cs[*cis*-α-Co(edda) $(NO_2)_2]\}_2 \cdot 3H_2O$ (**II**)

| | |
|---|---|
| Space Group | $C2/c$(No. 15) |
| Cell Constants | $a$ = 19.304(6) Å |
| | $b$ = 10.992 (4) |
| | $c$ = 13.890(5) |
| | β = 106.42(3)° |
| Cell Volume | $V$ = 2827.11 $Å^3$ |
| Molecular Formula | $Cs_2Co_2O_{11}N_8C_{12}H_{14}$ |
| Molecular Weight | 829.97 $gm\text{-}mole^{-1}$ |
| Density (calc; z = 4 mol/cell) | 1.950 $gm\text{-}cm^{-3}$ |
| Radiation Employed | $MoK_\alpha$ (λ = 0.71073 Å) |
| Absorption Coefficient | μ = 37.482 $cm^{-1}$ |
| Relative Transmission Coefficients | 0.5876 to 0.9984 |
| Data Collection Range | 4° ≤ 2Θ ≤ 60° |
| Scan Width | ΔΘ = 1.00 + 0.35tanΘ |
| Total Data Collected | 4190 |
| Data Used In Refinement* | 2605 |
| F(000) | 1576 |
| $R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$ | 0.034 |
| $Rw = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$ | 0.035 |
| Weights Used | $w = [\sigma(F_o)]^{-2}$ |

* The difference between this number and the total is due to subtraction of 1585 systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, were symmetry related, standards or did not meet the criterion that I ≥ 2.5σ(I).

TABLE III Summary of data collection and processing parameters for racemic Rb[*cis*-α-Co(edda)$(NO_2)_2$] · $H_2O$ (**III**)

| | |
|---|---|
| SpaceGroup | $P\bar{1}$(No.2) |
| Cell Constants | $a = 7.348(1)$ Å |
| | $b = 9.986\,(2)$ |
| | $c = 11.102(3)$ |
| | $\alpha = 63.36(2)°$ |
| | $\beta = 66.23(2)$ |
| | $\gamma = 75.79(2)°$ |
| Cell Volume | $V = 664.27$ Å$^3$ |
| Molecular Formula | $RbCoO_9N_4C_6H_{12}$ |
| Molecular Weight | 428.58 gm-mole$^{-1}$ |
| Density (calc; z = 2 mol/cell) | 2.143 gm-cm$^{-3}$ |
| Radiation Employed | $MoK_\alpha$ ($\lambda = 0.71073$ Å) |
| Absorption Coefficient | $\mu = 48.8$ cm$^{-1}$ |
| Relative Transmission Coefficients | 0.1891 to 0.3565 |
| Data Collection Range | $4° \leq 2\Theta \leq 50°$ |
| ScanWidth | $\Delta\Theta = 1.00 + 0.35\tan\Theta$ |
| Total Data Collected | 2496 |
| Data Used In Refinement* | 1764 |
| F(000) | 423 |
| $R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$ | 0.045 |
| $R_w = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$ | 0.052 |
| Weights Used | $w = [\sigma(F_o)]^{-2}$ |

* The difference between this number and the total is due to subtraction of 732 systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, were symmetry related, standards or did not meet the criterion that $I \geq 2.5\sigma(I)$.

TABLE IV Summary of data collection and processing parameters for racemic $NH_4$[*cis*-α-Co(edda)$(NO_2)_2$] · $2H_2O$ (**IV**)

| | |
|---|---|
| Space Group | $C2/c$ (No. 15) |
| Cell Constants | $a = 23.240(14)$ Å |
| | $b = 7.101(9)$ |
| | $c = 20.948(17)$ |
| | $\beta = 122.11(7)°$ |
| Cell Volume | $V = 2928.18$ Å$^3$ |
| Molecular Formula | $CoO_{10}N_5C_6H_{18}$ |
| Molecular Weight | 379.17 gm-mole$^{-1}$ |
| Density (calc; z = 8 mol/cell) | 1.720 gm-cm$^{-3}$ |
| Radiation Employed | $MoK_\alpha$ ($\lambda = 0.71073$ Å) |
| Absorption Coefficient | $\mu = 12.30$ cm$^{-1}$ |
| Relative Transmission Coefficients | 0.6733 to 0.7570 |
| Data Collection Range | $4° \leq 2\Theta \leq 55°$ |
| Scan Width | $\Delta\Theta = 1.00 + 0.35\tan\Theta$ |
| Total Data Collected | 3474 |
| Data Used In Refinement* | 1639 |
| F(000) | 1572 |
| $R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$ | 0.045 |
| $R_w = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$ | 0.049 |
| Weights Used | $w = [\sigma(F_o)]^{-2}$ |

* The difference between this number and the total is due to subtraction of 1835 systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, were symmetry related, standards or did not meet the criterion that $I \geq 2.5\sigma(I)$.

The positions of the heaviest atoms were obtained from a Patterson map and the missing heavy atoms were found in difference maps. Heavy atoms were refined anisotropically until convergence and hydrogen atoms of the anions were added at fixed, idealized positions (N-H, C-H = 0.95 Å; B = 5.0 Å$^2$). Hydrogens of ammonium cations and waters were found in a final difference Fourier, where listed. Final $R$(F) and $R_w$(F) factors are listed in Tables I through IV. Final positional and equivalent-isotropic thermal parameters are given in Tables V through VIII. Distances, angles and selected torsional angles and hydrogen bonds (up to 2.75 Å long) are listed in Tables IX through XII.

TABLE V Positional parameters and their esd's for I

| *Atom* | *x* | *y* | *z* | *B*(Å$^2$) |
|---|---|---|---|---|
| Co | -0.00371(5) | 0.13131(2) | -0.24835(2) | 1.599(7) |
| O1 | 0.2897(3) | 0.3079(1) | -0.1093(1) | 3.24(5) |
| O2 | 0.1699(2) | 0.1839(1) | -0.1585(1) | 2.27(4) |
| O3 | -0.4433(3) | 0.0026(1) | -0.3539(1) | 3.07(5) |
| O4 | -0.1894(2) | 0.0816(1) | -0.3356(1) | 2.03(4) |
| O5 | 0.2951(3) | 0.1818(1) | -0.3206(1) | 3.13(5) |
| O6 | 0.1425(3) | 0.0789(1) | -0.3886(1) | 3.94(5) |
| O7 | 0.2580(3) | 0.0128(1) | -0.1749(2) | 4.22(5) |
| O8 | -0.0114(3) | -0.0417(1) | -0.2148(2) | 3.62(5) |
| N1 | -0.0899(3) | 0.2489(1) | -0.2889(1) | 1.87(4) |
| N2 | -0.1955(3) | 0.1300(1) | -0.1719(1) | 1.90(4) |
| N3 | 0.1657(3) | 0.1300(1) | -0.3280(2) | 2.29(5) |
| N4 | 0.0919(3) | 0.0214(1) | -0.2075(2) | 2.37(5) |
| C1 | -0.2729(4) | 0.2581(2) | -0.2619(2) | 2.36(6) |
| C2 | -0.2626(4) | 0.2195(2) | -0.1726(2) | 2.52(6) |
| C3 | 0.0526(4) | 0.3087(2) | -0.2385(2) | 2.53(6) |
| C4 | 0.1809(4) | 0.2647(2) | -0.1627(2) | 2.30(6) |
| C5 | -0.3465(4) | 0.0709(2) | -0.2158(2) | 2.31(6) |
| C6 | -0.3302(4) | 0.0488(2) | -0.3081(2) | 2.08(5) |
| C7 | -0.1159(4) | 0.2648(2) | -0.3865(2) | 2.42(6) |
| C8 | -0.1798(4) | 0.3536(2) | -0.4163(2) | 3.44(7) |
| C9 | -0.1255(4) | 0.1028(2) | -0.0780(2) | 3.09(7) |
| C10 | -0.2681(5) | 0.1082(2) | -0.0197(2) | 4.26(8) |
| K | -0.26671(8) | 0.04700(4) | -0.51621(4) | 2.49(1) |
| Owl | -0.9006(3) | 0.0942(1) | -0.5954(2) | 3.75(5) |
| Ow2 | -0.5657(3) | 0.1515(1) | -0.4952(1) | 3.95(5) |
| Hw1 | -0.5000 | 0.3632 | -0.1132 | 5* |
| Hw2 | -0.4492 | 0.4316 | -0.0664 | 5* |
| Hw3 | -0.0996 | 0.3417 | 0.0683 | 5* |
| Hw4 | -0.0488 | 0.2949 | 0.0000 | 5* |
| H1 | -0.3662 | 0.2300 | -0.3034 | 5* |
| H2 | -0.3030 | 0.3166 | -0.2599 | 5* |
| H3 | -0.3826 | 0.2203 | -0.1584 | 5* |
| H4 | -0.1788 | 0.2515 | -0.1300 | 5* |
| H5 | -0.0098 | 0.3536 | -0.2156 | 5* |
| H6 | 0.1250 | 0.3311 | -0.2774 | 5* |
| H7 | -0.4634 | 0.0974 | -0.2175 | 5* |
| H8 | -0.3397 | 0.0201 | -0.1822 | 5* |
| H9 | -0.2060 | 0.2257 | -0.4159 | 5* |

TABLE V (*Continued*)

| *Atom* | *x* | *y* | *z* | *B*($Å^2$) |
|---|---|---|---|---|
| H10 | −0.0003 | 0.2547 | −0.4033 | 5* |
| H11 | −0.1923 | 0.3577 | −0.4784 | 5* |
| H12 | −0.2963 | 0.3648 | −0.4008 | 5* |
| H13 | −0.0906 | 0.3938 | −0.3883 | 5* |
| H14 | −0.0231 | 0.1379 | −0.0533 | 5* |
| H15 | −0.0849 | 0.0455 | −0.0783 | 5* |
| H16 | −0.2132 | 0.0900 | 0.0382 | 5* |
| H17 | −0.3092 | 0.1652 | −0.0178 | 5* |
| H18 | −0.3710 | 0.0727 | −0.0428 | 5* |

* Hydrogen atoms were added at idealized positions with fixed thermal parameters of 5.0 $Å^2$. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) * $[a^2*\beta_{11} + b^2*\beta_{22} + C^2*\beta_{33} + ab(\cos\gamma)*\beta_{12} + ac(\cos\beta)*\beta_{13} + bc(\cos\alpha)*\beta_{23}]$

TABLE VI Atomic parameters *x,y,z* and biso for compound (II). e.s.ds. refer to the last digit printed

| | *x* | *y* | *z* | *biso* |
|---|---|---|---|---|
| Cs | 0.370537(20) | 0.05798(3) | 0.37498(3) | 4.211(16) |
| Co | 0.37981(3) | −0.34078(5) | 0.44461(4) | 1.574(19) |
| O1 | 0.47810(19) | −0.1504(3) | 0.4787(3) | 3.40(15) |
| O2 | 0.48459(25) | −0.2652(4) | 0.3577(4) | 4.67(22) |
| O3 | 0.3181(3) | −0.1978(4) | 0.2796(3) | 4.68(21) |
| O4 | 0.21072(21) | 0.1152(4) | 0.2453(3) | 3.63(16) |
| O5 | 0.33527(16) | −0.2087(3) | 0.49168(23) | 2.24(12) |
| O6 | 0.42273(15) | −0.4776(3) | 0.40333(23) | 1.94(12) |
| O7 | 0.33991(20) | 0.0992(4) | 0.1270(3) | 3.81(16) |
| O8 | 0.40795(18) | 0.3271(3) | 0.3653(3) | 2.92(15) |
| N1 | 0.43362(18) | −0.3689(4) | 0.5865(3) | 2.11(14) |
| N2 | 0.30771(18) | −0.4556(4) | 0.4676(3) | 2.02(14) |
| N3 | 0.45684(20) | −0.2403(4) | 0.4249(3) | 2.45(15) |
| N4 | 0.32208(22) | −0.3035(4) | 0.3102(3) | 2.50(16) |
| C1 | 0.4029(3) | −0.4786(5) | 0.6213(4) | 2.70(19) |
| C2 | 0.3217(3) | −0.4729(5) | 0.5768(4) | 2.69(19) |
| C3 | 0.42590(24) | −0.2575(5) | 0.6430(3) | 2.46(18) |
| C4 | 0.36236(23) | −0.1823(5) | 0.5849(4) | 2.39(17) |
| C5 | 0.31406(23) | 0.4283(4) | 0.4158(4) | 2.36(18) |
| C6 | 0.38603(23) | 0.4225(4) | 0.3924(3) | 3(15) |
| Ow1 | 0.3611(3) | 0.1875(6) | 0.5787(4) | 6.7(3) |
| Ow2 | 0.50000 | −0.0078(7) | 0.25000 | 8.2(6) |
| Hw1 | 0.344 | 0.188 | 0.641 | 3.2 |
| Hw2 | 0.404 | 0.222 | 0.603 | 3.2 |
| H1 | 0.482 | −0.382 | 0.587 | 3.2 |
| H2 | 0.421 | −0.550 | 0.599 | 3.2 |
| H3 | 0.415 | −0.479 | 0.693 | 3.2 |
| H4 | 0.303 | −0.407 | 0.605 | 3.2 |
| H5 | 0.300 | −0.546 | 0.590 | 3.2 |
| H6 | 0.264 | −0.466 | 0.416 | 3.2 |
| H7 | 0.418 | −0.281 | 0.705 | 3.2 |
| H8 | 0.469 | −0.211 | 0.655 | 3.2 |
| H9 | 0.311 | 0.362 | 0.458 | 3.2 |
| H10 | 0.276 | 0.423 | 0.355 | 3.2 |

Biso is the mean of the principal axes of the thermal ellipsoid.

TABLE VII Atomic parameters *x,y,z* and biso for compound (III). e.s.ds. refer to the last digit printed

| | *x* | *y* | *z* | *biso* |
|---|---|---|---|---|
| Rb | 0.88412(14) | 0.74646(9) | 0.62156(9) | 3.38(5) |
| Co | 0.59775(14) | 0.24174(10) | 0.75933(10) | 1.20(4) |
| O1 | 0.7910(8) | 0.4419(6) | 0.7629(7) | 3.0(3) |
| O2 | 1.0289(8) | 0.6529(6) | 0.3902(6) | 2.6(3) |
| O3 | 0.8979(8) | 1.0179(6) | 0.8126(6) | 2.9(3) |
| O4 | 0.8233(9) | 1.0369(6) | 0.6387(7) | 3.1(3) |
| O5 | 0.4285(7) | 0.8291(5) | 1.0456(5) | 1.76(23) |
| O6 | 0.3933(7) | 0.6829(5) | 0.4333(5) | 1.76(24) |
| O7 | 0.5400(9) | 0.7620(7) | 0.8610(6) | 3.3(3) |
| O8 | 0.5100(8) | 0.7155(6) | 0.5742(6) | 2.9(3) |
| N1 | 0.3999(9) | 0.4054(6) | 0.7913(6) | 1.6(3) |
| N2 | 0.3712(9) | 0.1313(6) | 0.8082(6) | 1.7(3) |
| N3 | 0.8120(9) | 0.3582(6) | 0.7028(7) | 1.8(3) |
| N4 | 0.7921(9) | 1.0776(6) | 0.7359(6) | 1.9(3) |
| C1 | 0.2096(11) | 0.3805(8) | 0.7878(8) | 2.1(4) |
| C2 | 0.1853(10) | 0.2138(9) | 0.8690(8) | 2.1(4) |
| C3 | 0.6259(12) | 0.5946(9) | 1.0685(8) | 2.1(4) |
| C4 | 0.5241(10) | 0.7375(8) | 0.9841(8) | 2.0(4) |
| C5 | 0.6154(11) | 0.8754(8) | 0.3255(8) | 2.1(4) |
| C6 | 0.4996(11) | 0.7483(8) | 0.4558(8) | 2.0(3) |
| Owl | 1.1136(10) | 0.7331(7) | 0.7942(8) | 4.6(4) |
| H1 | 0.451 | 0.487 | 0.700 | 2.6 |
| H2 | 0.101 | 0.435 | 0.833 | 3.0 |
| H3 | 0.216 | 0.411 | 0.692 | 3.0 |
| H4 | 0.076 | 0.190 | 0.859 | 2.8 |
| H5 | 0.162 | 0.186 | 0.967 | 2.8 |
| H6 | 0.390 | 0.034 | 0.877 | 2.4 |
| H7 | 0.570 | 0.511 | 1.081 | 3.1 |
| H8 | 0.765 | 0.591 | 1.012 | 3.1 |
| H9 | 0.746 | 0.867 | 0.327 | 3.0 |
| H10 | 0.549 | 0.969 | 0.329 | 3.0 |
| Hwl | 1.056 | 0.851 | 0.799 | 1.9 |
| Hw2 | 1.225 | 0.736 | 0.749 | 1.9 |

Biso is the mean of the principal axes of the thermal ellipsoid.

TABLE VIII Atomic parameters *x,y,z* and biso for compound (IV) e.s.ds. refer to the last digit printed

| | *x* | *y* | *z* | *biso* |
|---|---|---|---|---|
| Co | 0.30216(4) | 0.24427(16) | 0.15374(4) | 1.64(3) |
| O1 | 0.3410(3) | −0.0512(8) | 0.2550(3) | 4.1(3) |
| O2 | 0.23503(24) | −0.0021(7) | 0.1930(3) | 3.0(3) |
| O3 | 0.3579(3) | 0.0093(12) | 0.0967(4) | 7.2(4) |
| O4 | 0.4293(3) | 0.1239(15) | 0.1958(4) | 9.3(6) |
| O5 | 0.23340(22) | 0.1403(6) | 0.06059(22) | 2.35(22) |
| O6 | 0.36622(23) | 0.3529(7) | 0.24652(22) | 2.67(25) |
| O7 | 0.12343(24) | 0.0938(8) | −0.0114(3) | 3.9(3) |
| O8 | 0.4457(3) | 0.5711(8) | 0.3008(3) | 4.7(3) |
| N | 0.4888(3) | −0.0549(10) | 0.3547(3) | 4.0(4) |
| N1 | 0.2283(3) | 0.3838(7) | 0.1513(3) | 2.0(3) |
| N2 | 0.3156(3) | 0.4688(7) | 0.1086(3) | 2.4(3) |
| N3 | 0.2919(3) | 0.0401(8) | 0.2063(3) | 2.4(3) |

TABLE VIII *(Continued)*

| | *x* | *y* | *z* | *biso* |
|---|---|---|---|---|
| N4 | 0.3712(3) | 0.1132(9) | 0.1477(3) | 2.5(3) |
| C1 | 0.2369(3) | 0.5843(10) | 0.1406(4) | 2.7(4) |
| C2 | 0.2569(4) | 0.5955(9) | 0.0833(3) | 2.7(4) |
| C3 | 0.1626(3) | 0.3060(9) | 0.0913(4) | 2.6(3) |
| C4 | 0.1721(3) | 0.1702(10) | 0.0427(3) | 2.6(3) |
| C5 | 0.3816(4) | 0.5534(11) | 0.1665(4) | 3.4(4) |
| C6 | 0.3996(3) | 0.4897(10) | 0.2445(4) | 3.0(3) |
| Ow1 | 0.4291(3) | 0.2254(10) | 0.5031(3) | 5.1(4) |
| Ow2 | 0.4856(3) | 0.3070(9) | 0.4185(3) | 4.7(3) |
| Hw1 | 0.4092(6) | 0.3125(17) | 0.5121(6) | 1.40(22) |
| Hw2 | 0.4438(6) | 0.2708(17) | 0.4756(6) | 1.40(22) |
| Hw3 | 0.5244(6) | 0.3681(17) | 0.4470(6) | 1.40(22) |
| Hw4 | 0.4562(6) | 0.2431(17) | 0.4423(6) | 1.40(22) |
| H1 | 0.234 | 0.364 | 0.199 | 2.8 |
| H2 | 0.195 | 0.650 | 0.123 | 3.3 |
| H3 | 0.271 | 0.638 | 0.187 | 3.3 |
| H4 | 0.269 | 0.721 | 0.080 | 3.3 |
| H5 | 0.220 | 0.556 | 0.035 | 3.3 |
| H6 | 0.317 | 0.424 | 0.067 | 3.1 |
| H7 | 0.142 | 0.242 | 0.114 | 3.4 |
| H8 | 0.134 | 0.406 | 0.061 | 3.4 |
| H9 | 0.416 | 0.514 | 0.158 | 4.1 |
| H10 | 0.378 | 0.687 | 0.163 | 4.1 |
| H11 | 0.5188(6) | −0.1458(17) | 0.3943(6) | 1.40(22) |
| H12 | 0.5099(6) | 0.0208(17) | 0.3396(6) | 1.40(22) |
| H13 | 0.4264 (6) | −0.0585(17) | 0.3153(6) | 1.40(22) |
| H14 | 0.490 | 0.036 | 0.390 | 4.8 |

Biso is the mean of the principal axes of the thermal ellipsoid.

TABLE IX Bond distances (Å) and angles (°) for I

*A) Distances*

| *Atom1* | *Atom2* | *Distance* | *Atom1* | *Atom2* | *Distance* |
|---|---|---|---|---|---|
| Co | O2 | 1.879(1) | N2 | C5 | 1.501(2) |
| Co | O4 | 1.885(1) | N2 | C9 | 1.503(2) |
| Co | N1 | 2.016(1) | N2 | C9 | 1.503(2) |
| Co | N2 | 2.015(1) | C1 | C2 | 1.499(2) |
| Co | N3 | 1.920(1) | C3 | C4 | 1.515(2) |
| Co | N4 | 1.926(1) | C5 | C6 | 1.500(2) |
| O1 | C4 | 1.233(2) | C7 | C8 | 1.517(2) |
| O2 | C4 | 1.278(2) | C9 | C10 | 1.517(2) |
| O3 | C6 | 1.217(2) | Ow1 | Hw1 | 0.988(1) |
| O4 | C6 | 1.302(2) | Ow1 | Hw2 | 0.747(1) |
| O5 | N3 | 1.241(2) | Ow2 | Hw3 | 1.069(1) |
| O6 | N3 | 1.222(2) | Ow2 | Hw4 | 0.858(1) |
| O7 | N4 | 1.229(2) | K | O1 | 2.777(1) |
| O8 | N4 | 1.241(2) | K | O3 | 2.731(1) |
| N1 | C1 | 1.492(2) | K | O4 | 2.795(1) |
| N1 | C3 | 1.503(2) | K | O6 | 2.753(1) |
| N1 | C7 | 1.507(2) | K | Ow1 | 2.930(1) |
| N2 | C2 | 1.493(2) | K | Ow2 | 2.814(1) |

TABLE IX *(Continued)*

*B) Angles*

| *Atom1* | *Atom2* | *Atom3* | *Angle* |
|---|---|---|---|
| O2 | Co | O4 | 176.53(4) |
| O2 | Co | N1 | 87.06(5) |
| O2 | Co | N2 | 91.08(5) |
| O2 | Co | N3 | 92.89(5) |
| O2 | Co | N4 | 90.31(5) |
| O4 | Co | N1 | 91.28(5) |
| O4 | Co | N2 | 85.83(5) |
| O4 | Co | N3 | 90.18(5) |
| O4 | Co | N4 | 91.43(5) |
| N1 | Co | N2 | 88.89(5) |
| N1 | Co | N3 | 90.75(5) |
| N1 | Co | N4 | 176.90(5) |
| N2 | Co | N3 | 175.99(5) |
| N2 | Co | N4 | 92.81(5) |
| N3 | Co | N4 | 87.73(5) |
| Co | O2 | C4 | 116.2(1) |
| Co | O4 | C6 | 115.97(9) |
| Co | N1 | C1 | 104.20(9) |
| Co | N1 | C3 | 105.79(9) |
| Co | N1 | C7 | 115.69(9) |
| C1 | N1 | C3 | 111.4(1) |
| C1 | N1 | C7 | 109.0(1) |
| C3 | N1 | C7 | 110.6(1) |
| Co | N2 | C2 | 104.71(9) |
| Co | N2 | C5 | 106.22(9) |
| Co | N2 | C9 | 115.40(9) |
| C2 | N2 | C5 | 111.7(1) |
| C2 | N2 | C9 | 108.9(1) |
| C5 | N2 | C9 | 109.9(1) |
| Co | N3 | O5 | 121.1(1) |
| Co | N3 | O6 | 119.5(1) |
| O5 | N3 | O6 | 119.3(1) |
| Co | N4 | O7 | 119.9(1) |
| Co | N4 | O8 | 121.0(1) |
| O7 | N4 | O8 | 119.1(1) |
| N1 | C1 | C2 | 109.8(1) |
| N2 | C2 | C1 | 110.2(1) |
| N1 | C3 | C4 | 112.0(1) |
| O1 | C4 | O2 | 123.7(2) |
| O1 | C4 | C3 | 119.0(2) |
| O2 | C4 | C3 | 117.3(1) |
| N2 | C5 | C6 | 112.5(1) |
| O3 | C6 | O4 | 122.7(2) |
| O3 | C6 | C5 | 121.2(1) |
| O4 | C6 | C5 | 116.1(1) |
| N1 | C7 | C8 | 115.3(1) |
| N2 | C9 | C10 | 114.7(1) |
| Hw1 | Ow1 | Hw2 | 97.1(1) |
| Hw3 | Ow2 | Hw4 | 92.7(1) |

TABLE IX *(Continued)*

*C) Torsional Angles*

| *Atom1* | *Atom2* | *Atom3* | *Atom4* | *Angle* |
|---|---|---|---|---|
| O4 | Co | O2 | C4 | −68.6 |
| N1 | Co | O2 | C4 | −7.0 |
| N2 | Co | O2 | C4 | −95.8 |
| N3 | Co | O2 | C4 | 83.6 |
| N4 | Co | O2 | C4 | 171.4 |
| O2 | Co | O4 | C6 | −43.9 |
| O2 | Co | O4 | K | 139.0 |
| N1 | Co | O4 | C6 | −105.3 |
| N1 | Co | O4 | K | 77.6 |
| N2 | Co | O4 | C6 | −16.5 |
| N2 | Co | O4 | K | 166.4 |
| N3 | Co | O4 | C6 | 163.9 |
| N3 | Co | O4 | K | −13.2 |
| N4 | Co | O4 | C6 | 76.2 |
| N4 | Co | O4 | K | −100.9 |
| O2 | Co | N1 | C1 | −106.6 |
| O2 | Co | N1 | C3 | 11.0 |
| O2 | Co | N1 | C7 | 133.7 |
| O4 | Co | N1 | C1 | 70.3 |
| O4 | Co | N1 | C3 | −172.1 |
| O4 | Co | N1 | C7 | −49.3 |
| N2 | Co | N1 | C1 | −15.5 |
| O4 | Co | N3 | O6 | −24.1 |
| N1 | Co | N3 | O5 | 62.4 |
| N1 | Co | N3 | O6 | −115.4 |
| N2 | Co | N3 | O5 | 147.2 |
| N2 | Co | N3 | O6 | −30.6 |
| N4 | Co | N3 | O5 | −114.9 |
| N4 | Co | N3 | O6 | 67.3 |
| O2 | Co | N4 | O7 | −33.0 |
| O2 | Co | N4 | O8 | 148.1 |
| O4 | Co | N4 | O7 | 150.0 |
| O4 | Co | N4 | O8 | −28.9 |
| N1 | Co | N4 | O7 | −0.9 |
| N1 | Co | N4 | O8 | −179.9 |
| N2 | Co | N4 | O7 | −124.1 |
| N2 | Co | N4 | O8 | 57.0 |
| N3 | Co | N4 | O7 | 59.9 |
| N3 | Co | N4 | O8 | −119.0 |
| Co | O2 | C4 | O1 | −179.1 |
| Co | O2 | C4 | C3 | 0.6 |
| Co | O4 | C6 | O3 | −167.3 |
| Co | O4 | C6 | C5 | 12.7 |
| K | O4 | C6 | O3 | 10.8 |
| N2 | Co | N1 | C3 | 102.1 |
| N2 | Co | N1 | C7 | −135.1 |
| N3 | Co | N1 | C1 | 160.5 |
| N3 | Co | N1 | C3 | −81.9 |
| N3 | Co | N1 | C7 | 40.9 |

TABLE IX (*Continued*)

*C) Torsional Angles*

| *Atom 1* | *Atom 2* | *Atom 3* | *Atom 4* | *Angle* |
|---|---|---|---|---|
| N4 | Co | N1 | C1 | −138.7 |
| N4 | Co | N1 | C3 | −21.1 |
| N4 | Co | N1 | C7 | 101.6 |
| O2 | Co | N2 | C2 | 75.5 |
| O2 | Co | N2 | C5 | −166.2 |
| O2 | Co | N2 | C9 | −44.2 |
| O4 | Co | N2 | C2 | −102.9 |
| O4 | Co | N2 | C5 | 15.4 |
| O4 | Co | N2 | C9 | 137.4 |
| N1 | Co | N2 | C2 | −11.6 |
| N1 | Co | N2 | C5 | 106.7 |
| N1 | Co | N2 | C9 | −131.3 |
| N3 | Co | N2 | C2 | −96.4 |
| N3 | Co | N2 | C5 | 21.9 |
| N3 | Co | N2 | C9 | 143.8 |
| N4 | Co | N2 | C2 | 165.9 |
| N4 | Co | N2 | C5 | −75.8 |
| N4 | Co | N2 | C9 | 46.1 |
| K | O4 | C6 | C5 | −169.2 |
| Co | O4 | K | Ow2 | −120.5 |
| C6 | O4 | K | Ow2 | 62.2 |
| Co | N1 | C1 | C2 | 40.2 |
| C3 | N1 | C1 | C2 | −73.5 |
| C7 | N1 | C1 | C2 | 164.2 |
| Co | N1 | C3 | C4 | −13.0 |
| C1 | N1 | C3 | C4 | 99.6 |
| C7 | N1 | C3 | C4 | −139.0 |
| Co | N1 | C7 | C8 | −179.7 |
| C1 | N1 | C7 | C8 | 63.3 |
| C3 | N1 | C7 | C8 | −59.5 |
| Co | N2 | C2 | C1 | 37.1 |
| C5 | N2 | C2 | C1 | −77.4 |
| C9 | N2 | C2 | C1 | 161.1 |
| Co | N2 | C5 | C6 | −12.8 |
| C2 | N2 | C5 | C6 | 100.8 |
| C9 | N2 | C5 | C6 | −138.2 |
| Co | N2 | C9 | C10 | 175.8 |
| C2 | N2 | C9 | C10 | 58.4 |
| C5 | N2 | C9 | C10 | −64.2 |
| N1 | C1 | C2 | N2 | −53.9 |
| N1 | C3 | C4 | O1 | −171.2 |
| O2 | Co | N3 | O5 | −24.7 |
| O2 | Co | N3 | O6 | 157.5 |
| O4 | Co | N3 | O5 | 153.6 |
| N1 | C3 | C4 | O2 | 9.1 |
| N2 | C5 | C6 | O3 | −178.8 |
| N2 | C5 | C6 | O4 | 1.2 |

*D) Selected List of Hydrogen Bonds*

| | | | | |
|---|---|---|---|---|
| O1–Hw1 | 1.79 | Ow1–Hw1 ... O1 | 155.3 | Ow1 at 1/2+x, 1/2−y, 1/2+z |
| O5–Hw3 | 2.05 | Ow2–Hw3 ... O5 | 169.7 | Ow2 at 1+x, y, z |
| O6–Hw3 | 2.47 | Ow2–Hw3 ... O6 | 123.2 | Ow2 at 1+x, y, z |

*No esd's are shown since hydrogen atoms were not refined

TABLE X Bond distances (Å) and bond angles (°) for compound (II)

*A. Bond Distances*

| | | | |
|---|---|---|---|
| Cs–Csa | 5.3718(15) | O3–N4 | 1.232(5) |
| Cs–O1 | 3.152(4) | O4–N4b | 1.231(5) |
| Cs–O1a | 3.217(3) | O5–C4 | 1.286(5) |
| Cs–O3 | 3.149(4) | O6–C6c | 1.290(5) |
| Cs–O4 | 3.168(3) | O7–C4d | 1.226(6) |
| Cs–O5 | 3.507(4) | O8–C6 | 1.228(5) |
| Cs–O7 | 3.356(4) | N1–Cl | 1.484(6) |
| Cs–O8 | 3.057(4) | N1–C3 | 1.484(6) |
| Cs–Owl | 3.219(6) | N2–C2 | 1.476(6) |
| Cs–Ow2 | 3.4979(19) | N2–C5c | 1.489(6) |
| Co–O5 | 1.894(3) | N4–O4e | 1.231(5) |
| Co–O6 | 1.882(3) | C1–C2 | 1.510(7) |
| Co–N1 | 1.974(3) | C3–C4 | 1.508(6) |
| Co–N2 | 1.969(4) | C4–O7f | 1.226(6) |
| Co–N3 | 1.929(4) | C5–N2g | 1.489(6) |
| Co–N4 | 1.925(4) | C5–C6 | 1.510(6) |
| O1–Csa | 3.217(3) | C6–O6g | 1.290(5) |
| O1–N3 | 1.236(5) | Ow2–Csh | 3.4979(19) |
| O2–N3 | 1.231(6) | | |

*B. Bond Angles*

| | | | |
|---|---|---|---|
| Csa–Cs–O1 | 32.88(6) | O5–Co–N2 | 91.48(15) |
| Csa–Cs–O1a | 32.13(7) | O5–Co–N3 | 92.93(15) |
| Csa–Cs–O3 | 100.85(8) | O5–Co–N4 | 88.72(15) |
| Csa–Cs–O4 | 173.91(7) | O6–Co–N1 | 91.56(14) |
| Csa–Cs–O5 | 76.66(5) | O6–Co–N2 | 85.86(14) |
| Csa–Cs–O7 | 123.83(7) | O6–Co–N3 | 89.64(15) |
| Csa–Cs–O8 | 94.03(6) | O6–Co–N4 | 93.29(15) |
| Csa–Cs–Ow1 | 79.04(10) | N1–Co–N2 | 86.16(15) |
| Csa–Cs–Ow2 | 66.86(4) | N1–Co–N3 | 91.36(16) |
| O1–Cs–O1a | 65.01(9) | N1–Co–N4 | 175.02(15) |
| O1–Cs–O3 | 68.52(10) | N2–Co–N3 | 174.79(15) |
| O1–Cs–O4 | 144.54(10) | N2–Co–N4 | 93.02(16) |
| O1–Cs–O5 | 50.96(8) | N3–Co–N4 | 89.85(17) |
| O1–Cs–O7 | 117.95(10) | Cs–O1–Csa | 114.99(11) |
| O1–Cs–O8 | 126.19(9) | Cs–O1–N3 | 103.9(3) |
| O1–Cs–Ow1 | 96.48(12) | Csa–O1–N3 | 136.3(3) |
| O1–Cs–Ow2 | 66.79(11) | Cs–O3–N4 | 135.8(3) |
| O1a–Cs–O3 | 132.29(10) | Cs–O4–N4b | 138.4(3) |
| Ola–Cs–O4 | 149.57(10) | Cs–O5–Co | 108.38(13) |
| Ola–Cs–O5 | 103.41(8) | Cs–O5–C4 | 101.6(3) |
| O1a–Cs–O7 | 118.05(9) | Co–O5–C4 | 115.2(3) |
| O1a–Cs–O8 | 62.54(9) | Co–O6–C6c | 116.3(3) |
| O1a–Cs–Ow1 | 64.65(11) | Cs–O7–C4d | 127.3(3) |
| Ola–Cs–Ow2 | 74.34(9) | Cs–O8–C6 | 135.1(3) |
| O3–Cs–O4 | 78.12(11) | Co–N1–Cl | 107.9(3) |
| O3–Cs–O5 | 50.70(9) | Co–N1–C3 | 107.2(3) |
| O3–Cs–O7 | 75.39(10) | C1–N1–C3 | 112.8(3) |
| O3–Cs–O8 | 153.83(10) | Co–N2–C2 | 108.4(3) |
| O3–Cs–Ow1 | 132.26(13) | Co–N2–C5c | 108.1(3) |
| O3–Cs–Ow2 | 78.22(15) | C2–N2–C5c | 111.8(4) |
| O4–Cs–O5 | 98.31(9) | Co–N3–O1 | 120.8(3) |
| O4–Cs–O7 | 61.89(9) | Co–N3–O2 | 119.9(3) |

TABLE X (*Continued*)

*B. Bond Angles*

| | | | |
|---|---|---|---|
| O4–Cs–O8 | 89.21(10) | O1–N3–O2 | 119.4(4) |
| O4–Cs–Ow1 | 97.16(12) | Co–N4–O3 | 119.7(3) |
| O4–Cs–Ow2 | 118.47(8) | Co–N4–O4e | 120.5(3) |
| O5–Cs–O7 | 125.90(8) | O3–N4–O4e | 119.8(4) |
| O5–Cs–O8 | 155.20(8) | N1–C1–C2 | 107.1(3) |
| O5–Cs–Ow1 | 84.05(11) | N2–C2–C1 | 107.1(3) |
| O5–Cs–Ow2 | 108.37(13) | N1–C3–C4 | 111.0(3) |
| O7–Cs–O8 | 78.45(9) | O5–C4–O7f | 123.5(4) |
| O7–Cs–Ow1 | 143.66(13) | O5–C4–C3 | 116.8(4) |
| O7–Cs–Ow2 | 57.42(8) | O7f–C4–C3 | 119.7(4) |
| O8–Cs–Ow1 | 71.53(12) | N2g–C5–C6 | 110.3(3) |
| O8–Cs–Ow2 | 88.20(14) | O6g–C6–O8 | 122.6(4) |
| Ow1–Cs–Ow2 | 138.92(10) | O6g–C6–C5 | 116.4(4) |
| O5–Co–O6 | 176.75(14) | O8–C6–C5 | 121.0(4) |
| O5–Co–N1 | 86.39(14) | Cs–Ow2–Csh | 156.12(25) |

*C. Torsion angles*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O3 | Cs | O1 | N3 | 9.3(2) | O4 | Cs | O1 | N3 | 30.3(2) |
| O5 | Cs | O1 | N3 | 65.5(2) | O7 | Cs | O1 | N3 | −49.6(2) |
| O8 | Cs | O1 | N3 | −145.8(3) | Ow1 | Cs | O1 | N3 | 142.4(3) |
| Ow2 | Cs | O1 | N3 | −76.7(2) | O1 | Cs | O3 | N4 | 32.3(2) |
| O4 | Cs | O3 | N4 | −135.5(3) | O5 | Cs | O3 | N4 | −24.2(2) |
| O7 | Cs | O3 | N4 | 160.8(3) | O8 | Cs | O3 | N4 | 161.9(3) |
| Ow1 | Cs | O3 | N4 | −46.6(2) | Ow2 | Cs | O3 | N4 | 101.7(3) |
| O1 | Cs | O5 | Co | −46.8(1) | O1 | Cs | O5 | C4 | 75.0(2) |
| O3 | Cs | O5 | Co | 46.3(1) | O3 | Cs | O5 | C4 | 168.1(3) |
| O4 | Cs | O5 | Co | 113.5(1) | O4 | Cs | O5 | C4 | −124.7(2) |
| O7 | Cs | O5 | Co | 52.3(1) | O7 | Cs | O5 | C4 | 174.1(3) |
| O8 | Cs | O5 | Co | −140.1(1) | O8 | Cs | O5 | C4 | −18.3(2) |
| Ow1 | Cs | O5 | Co | −150.1(2) | Ow1 | Cs | O5 | C4 | −28.3(2) |
| Ow2 | Cs | O5 | Co | −10.3(1) | Ow2 | Cs | O5 | C4 | 111.5(2) |
| O1 | Cs | O8 | C6 | −122.0(3) | O3 | Cs | O8 | C6 | 120.6(3) |
| O4 | Cs | O8 | C6 | 60.3(2) | O5 | Cs | O8 | C6 | −48.1(2) |
| O7 | Cs | O8 | C6 | 121.7(3) | Ow1 | Cs | O8 | C6 | −37.5(2) |
| Ow2 | Cs | O8 | C6 | 178.8(3) | O6 | Co | O5 | Cs | 172.5(1) |
| O6 | Co | O5 | C4 | 59.4(2) | N1 | Co | O5 | Cs | 121.6(1) |
| N1 | Co | O5 | C4 | 8.6(2) | N2 | Co | O5 | Cs | −152.3(2) |
| N2 | Co | O5 | C4 | 94.7(3) | N3 | Co | O5 | Cs | 30.4(1) |
| N3 | Co | O5 | C4 | −82.6(2) | N4 | Co | O5 | Cs | −59.3(1) |
| N4 | Co | O5 | C4 | −172.3(3) | O5 | Co | N1 | C1 | 106.4(3) |
| O5 | Co | N1 | C3 | −15.4(2) | O6 | Co | N1 | C1 | −71.1(2) |
| O6 | Co | N1 | C3 | 167.1(3) | N2 | Co | N1 | C1 | 14.6(2) |
| N2 | Co | N1 | C3 | −107.1(3) | N3 | Co | N1 | C1 | −160.8(3) |
| N3 | Co | N1 | C3 | 77.5(2) | N4 | Co | N1 | C1 | 95.3(3) |
| N4 | Co | N1 | C3 | −26.5(2) | O5 | Co | N2 | C2 | −71.9(2) |
| O6 | Co | N2 | C2 | 106.2(3) | N1 | Co | N2 | C2 | 14.4(2) |
| N3 | Co | N2 | C2 | 76.0(2) | N4 | Co | N2 | C2 | −160.7(3) |
| O5 | Co | N3 | O1 | 30.5(2) | O5 | Co | N3 | O2 | −149.1(3) |
| O6 | Co | N3 | O1 | −147.5(3) | O6 | Co | N3 | O2 | 32.9(2) |
| N1 | Co | N3 | O1 | −56.0(2) | N1 | Co | N3 | O2 | 124.5(3) |
| N2 | Co | N3 | O1 | −117.4(3) | N2 | Co | N3 | O2 | 63.1(3) |
| N4 | Co | N3 | O1 | 119.2(3) | N4 | Co | N3 | O2 | −60.4(3) |
| O5 | Co | N4 | O3 | 47.8(2) | O6 | Co | N4 | O3 | −134.7(3) |

TABLE X (*Continued*)

*C. Torsion angles*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N1 | Co | N4 | O3 | 58.9(2) | N2 | Co | N4 | O3 | 139.2(3) |
| N3 | Co | N4 | O3 | -45.1(2) | Cs | O1 | N3 | Co | -84.8(2) |
| Cs | O1 | N3 | O2 | 94.7(3) | Cs | O3 | N4 | Co | -7.1(1) |
| Cs | O5 | C4 | C3 | -115.9(3) | Co | O5 | C4 | C3 | 1.0(2) |
| Cs | O8 | C6 | C5 | -17.8(2) | Co | N1 | C1 | C2 | -40.0(2) |
| C3 | N1 | C1 | C2 | 78.2(3) | Co | N1 | C3 | C4 | 19.0(2) |
| C1 | N1 | C3 | C4 | -99.6(4) | Co | N2 | C2 | C1 | -39.9(2) |
| N1 | C1 | C2 | N2 | 52.8(3) | N1 | C3 | C4 | O5 | -14.1(2) |

TABLE XI Bond distances (Å) and bond angles (°) for compound (III)

*A. Bond Distances*

| | | | |
|---|---|---|---|
| Rb-Rba | 4.9087(16) | O4-N4 | 1.238(9) |
| Rb-O1 | 2.838(6) | O5-Cob | 1.893(5) |
| Rb-O2 | 2.840(6) | O5-C4 | 1.286(9) |
| Rb-O4 | 2.905(6) | O6-Coc | 1.901(5) |
| Rb-O4a | 3.053(6) | O6-C6 | 1.281(9) |
| Rb-O7 | 2.871(6) | O7-C4 | 1.233(9) |
| Rb-O8 | 3.108(6) | O8-C6 | 1.239(9) |
| Rb-Owl | 2.966(8) | N1-C1 | 1.496(9) |
| Co-O5b | 1.893(5) | N1-C3b | 1.527(9) |
| Co-O6c | 1.901(5) | N2-C2 | 1.484(10) |
| Co-N1 | 1.960(6) | N2-C5c | 1.480(10) |
| Co-N2 | 1.980(6) | N3-O2e | 1.229(8) |
| Co-N3 | 1.916(6) | N4-Cof | 1.930(6) |
| Co-N4d | 1.930(6) | C1-C2 | 1.512(11) |
| O1-N3 | 1.235(8) | C3-N1b | 1.527(9) |
| O2-N3e | 1.229(8) | C3-C4 | 1.511(11) |
| O3-N4 | 1.240(8) | C5-N2c | 1.480(10) |
| O4-Rba | 3.053(6) | C5-C6 | 1.521(10) |

*B. Bond Angles*

| | | | |
|---|---|---|---|
| Rba-Rb-O1 | 174.01(12) | N1-Co-N2 | 87.10(24) |
| Rba-Rb-O2 | 101.05(11) | N1-Co-N3 | 91.04(24) |
| Rba-Rb-O4 | 35.52(12) | N1-Co-N4d | 178.1(3) |
| Rba-Rb-O4a | 33.56(10) | N2-Co-N3 | 176.50(24) |
| Rba-Rb-O7 | 103.77(13) | N2-Co-N4d | 93.17(24) |
| Rba-Rb-O8 | 115.48(11) | N3-Co-N4d | 88.78(25) |
| Rba-Rb-Owl | 77.87(13) | Rb-O1-N3 | 125.1(5) |
| O1-Rb-O2 | 78.06(16) | Rb-O2-N3e | 138.3(4) |
| O1-Rb-O4 | 147.10(17) | Rb-O4-Rba | 110.92(18) |
| O1-Rb-O4a | 143.14(16) | Rb-O4-N4 | 134.2(5) |
| O1-Rb-O7 | 79.78(17) | Rba-O4-N4 | 104.0(4) |
| O1-Rb-O8 | 70.09(16) | Cob-O5-C4 | 115.6(4) |
| O1-Rb-Owl | 97.82(18) | Coc-O6-C6 | 115.2(4) |
| O2-Rb-O4 | 133.59(17) | Rb-O7-C4 | 130.9(5) |
| O2-Rb-O4a | 69.64(15) | Rb-O8-C6 | 124.3(5) |
| O2-Rb-O7 | 143.80(17) | Co-N1-C1 | 107.9(4) |
| O2-Rb-O8 | 73.78(15) | Co-N1-C3b | 108.4(4) |
| O2-Rb-Owl | 126.41(17) | C1-N1-C3b | 111.0(6) |
| O4-Rb-O4a | 69.08(16) | Co-N2-C2 | 107.4(4) |

TABLE XI (*Continued*)

*B. Bond Angles*

| | | | |
|---|---|---|---|
| O4–Rb–O7 | 68.43(17) | Co–N2–C5c | 106.7(4) |
| O4–Rb–O8 | 106.18(16) | C2–N2–C5c | 113.5(5) |
| O4–Rb–Ow1 | 71.71(18) | Co–N3–O1 | 119.5(5) |
| O4a–Rb–O7 | 137.08(16) | Co–N3–O2e | 120.4(5) |
| O4a–Rb–O8 | 115.24(16) | O1–N3–O2e | 120.0(6) |
| O4a–Rb–Ow1 | 87.75(18) | Cof–N4–O3 | 120.1(5) |
| O7–Rb–O8 | 71.90(16) | Cof–N4–O4 | 121.1(5) |
| O7–Rb–Ow1 | 84.69(18) | O3–N4–O4 | 118.6(6) |
| O8–Rb–Ow1 | 155.03(17) | N1–C1–C2 | 106.6(6) |
| O5b–Co–O6c | 176.37(21) | N2–C2–C1 | 108.6(6) |
| O5b–Co–N1 | 86.67(22) | N1b–C3–C4 | 109.9(6) |
| O5b–Co–N2 | 91.85(22) | O5–C4–O7 | 123.5(7) |
| O5b–Co–N3 | 91.01(24) | O5–C4–C3 | 117.7(6) |
| O5b–Co–N4d | 91.44(24) | O7–C4–C3 | 118.8(7) |
| O6c–Co–N1 | 90.34(23) | N2c–C5–C61 | 110.4(6) |
| O6c–Co–N2 | 85.94(22) | O6–C6–O8 | 124.1(7) |
| O6c–Co–N3 | 91.11(23) | O6–C6–C5 | 116.5(6) |
| O6c–Co–N4d | 91.56(24) | O8–C6–C5 | 119.4(7) |

*C. Torsion angles*

| | | | | |
|---|---|---|---|---|
| O2 | Rb | O1 | N3 | −6.3(5) |
| O4 | Rb | O1 | N3 | 159.7(7) |
| O7 | Rb | O1 | N3 | 144.9(7) |
| O8 | Rb | O1 | N3 | 70.6(6) |
| Ow1 | Rb | O1 | N3 | −132.0(7) |
| O1 | Rb | O4 | N4 | 33.2(5) |
| O2 | Rb | O4 | N4 | −165.7(7) |
| O7 | Rb | O4 | N4 | 49.0(5) |
| O8 | Rb | O4 | N4 | 111.4(6) |
| Owl | Rb | O4 | N4 | −42.5(5) |
| O1 | Rb | O7 | C4 | 85.6(7) |
| O2 | Rb | O7 | C4 | 138.5(7) |
| O4 | Rb | O7 | C4 | −85.8(7) |
| O8 | Rb | O7 | C4 | 157.8(7) |
| Ow1 | Rb | O7 | C4 | −13.4(6) |
| O1 | Rb | O8 | C6 | −119.5(7) |
| O2 | Rb | O8 | C6 | −36.7(6) |
| O4 | Rb | O8 | C6 | 94.9(7) |
| O7 | Rb | O8 | C6 | 155.0(8) |
| Owl | Rb | O8 | C6 | 176.2(8) |
| N2 | Co | N1 | C1 | −17.2(5) |
| N3 | Co | N1 | C1 | 159.8(8) |
| N1 | Co | N2 | C2 | −11.4(5) |
| N3 | Co | N2 | C2 | −70.1(6) |
| N1 | Co | N3 | O1 | 36.1(5) |
| N2 | Co | N3 | O1 | 94.7(7) |
| Rb | O1 | N3 | Co | −131.9(6) |
| Rb | O4 | N4 | O3 | 47.3(6) |
| Rb | O7 | C4 | O5 | 130.0(9) |
| Rb | O7 | C4 | C3 | −48.3(6) |
| Rb | O8 | C6 | O6 | 149.3(9) |
| Rb | O8 | C6 | C5 | −31.8(5) |
| Co | N1 | C1 | C2 | 41.5(5) |

TABLE XI (*Continued*)

*C. Torsion angles*

| | | | | |
|---|---|---|---|---|
| Co | N2 | C2 | C1 | 37.8(5) |
| N1 | C1 | C2 | N2 | −52.6(7) |
| N1 | C3 | C4 | O5 | −2.8(5) |
| N2 | C5 | C6 | O6 | 16.8(5) |

TABLE XII Bond distances (Å) and angles (°) for compound (IV)

*A. Bond Distances*

| | | | |
|---|---|---|---|
| Co–O5 | 1.895(4) | O6–C6 | 1.258(9) |
| Co–O6 | 1.874(4) | O7–C4 | 1.223(8) |
| Co–N1 | 1.960(5) | O8–C6 | 1.236(8) |
| Co–N2 | 1.962(5) | N1–C1 | 1.471(9) |
| Co–N3 | 1.911(5) | N1–C3 | 1.475(8) |
| Co–N4 | 1.916(6) | N2–C2 | 1.478(9) |
| O1–N3 | 1.235(7) | N2–C5 | 1.485(9) |
| O2–N3 | 1.234(7) | C1–C2 | 1.502(10) |
| O3–N4 | 1.196(8) | C3–C4 | 1.501(9) |
| O4–N4 | 1.183(8) | C5–C6 | 1.524(10) |
| O5–C4 | 1.284(8) | | |

*B. Bond Angles*

| | | | |
|---|---|---|---|
| O5–Co–O6 | 176.70(20) | Co–N2–C2 | 108.3(4) |
| O5–Co–N1 | 85.55(20) | Co–N2–C5 | 107.2(4) |
| O5–Co–N2 | 94.81(20) | C2–N2–C5 | 113.8(5) |
| O5–Co–N3 | 90.17(22) | Co–N3–O1 | 122.1(4) |
| O5–Co–N4 | 91.15(22) | Co–N3–O2 | 120.0(4) |
| O6–Co–N1 | 91.20(21) | O1–N3–O2 | 117.9(5) |
| O6–Co–N2 | 85.58(21) | Co–N4–O3 | 122.1(5) |
| O6–Co–N3 | 89.31(22) | Co–N4–O4 | 122.0(5) |
| O6–Co–N4 | 92.12(22) | O3–N4–O4 | 115.8(6) |
| N1–Co–N2 | 86.47(22) | N1–C1–C2 | 107.4(5) |
| N1–Co–N3 | 91.30(22) | N2–C2–C1 | 107.4(5) |
| N1–Co–N4 | 175.34(21) | N1–C3–C4 | 111.1(5) |
| N2–Co–N3 | 174.37(22) | O5–C4–O7 | 122.2(6) |
| N2–Co–N4 | 90.53(23) | O5–C4–C3 | 116.7(5) |
| N3–Co–N4 | 92.00(23) | O7–C4–C3 | 121.2(6) |
| Co–O5–C4 | 115.7(4) | N2–C5–C6 | 109.3(5) |
| Co–O6–C6 | 116.5(4) | O6–C6–O8 | 124.5(7) |
| Co–N1–C1 | 107.7(4) | O6–C6–C5 | 116.3(6) |
| Co–N1–C3 | 109.2(4) | O8–C6–C5 | 119.2(7) |
| C1–N1–C3 | 113.3(5) | | |

*C. Torsion Angles*

| | | | | |
|---|---|---|---|---|
| O6 | Co | O5 | C4 | −1.5(3) |
| N2 | Co | O5 | C4 | −98.0(4) |
| N4 | Co | O5 | C4 | 171.3(4) |
| N1 | Co | O6 | C6 | −99.5(4) |
| N3 | Co | O6 | C6 | 169.2(4) |
| O5 | Co | N1 | C1 | −111.8(4) |
| O6 | Co | N1 | C1 | 68.8(3) |
| N2 | Co | N1 | C1 | −16.7(3) |

TABLE XII (*Continued*)

*C. Torsion Angles*

| | | | | |
|---|---|---|---|---|
| N3 | Co | N1 | C1 | 158.1(4) |
| N4 | Co | N1 | C1 | −66.8(3) |
| O5 | Co | N2 | C2 | 73.3(3) |
| O6 | Co | N2 | C2 | −103.4(4) |
| N1 | Co | N2 | C2 | −11.9(3) |
| N3 | Co | N2 | C2 | −78.7(3) |
| N4 | Co | N2 | C2 | 164.5(4) |
| O5 | Co | N3 | O1 | 130.2(4) |
| O6 | Co | N3 | O1 | −53.0(3) |
| N1 | Co | N3 | O1 | −144.2(4) |
| N2 | Co | N3 | O1 | −77.6(3) |
| N4 | Co | N3 | O1 | 39.1(3) |
| O5 | Co | N4 | O3 | −1.8(3) |
| O6 | Co | N4 | O3 | 177.8(5) |
| N1 | Co | N4 | O3 | −46.6(4) |
| N2 | Co | N4 | O3 | −96.6(4) |
| N3 | Co | N4 | O3 | 88.4(4) |
| Co | O5 | C4 | O7 | −171.7(6) |
| Co | O6 | C6 | O8 | −176.6(6) |
| Co | N1 | C1 | C2 | 41.4(3) |
| Co | N1 | C3 | C4 | −10.0(2) |
| Co | N2 | C2 | C1 | 37.5(3) |
| Co | N2 | C5 | C6 | −22.6(3) |
| N1 | C1 | C2 | N2 | −52.2(4) |
| N1 | C3 | C4 | O7 | −178.2(7) |
| N2 | C5 | C6 | O8 | −166.6(8) |
| N1 | Co | O5 | C4 | −11.9(3) |
| N3 | Co | O5 | C4 | 79.3(3) |
| O5 | Co | O6 | C6 | −109.9(4) |
| N2 | Co | O6 | C6 | −13.1(3) |
| N4 | Co | O6 | C6 | 77.3(4) |
| O5 | Co | N1 | C3 | 11.7(2) |
| O6 | Co | N1 | C3 | −167.7(4) |
| N2 | Co | N1 | C3 | 106.8(3) |
| N3 | Co | N1 | C3 | −78.4(3) |
| N4 | Co | N1 | C3 | 56.7(3) |
| O5 | Co | N2 | C5 | −163.5(4) |
| O6 | Co | N2 | C5 | 19.8(3) |
| N1 | Co | N2 | C5 | 111.2(4) |
| N3 | Co | N2 | C5 | 44.4(3) |
| N4 | Co | N2 | C5 | −72.3(3) |
| O5 | Co | N3 | O2 | −51.0(3) |
| O6 | Co | N3 | O2 | 125.7(4) |
| N1 | Co | N3 | O2 | 34.5(3) |
| N2 | Co | N3 | O2 | 101.1(4) |
| N4 | Co | N3 | O2 | −142.2(4) |
| O5 | Co | N4 | O4 | −178.5(5) |
| O6 | Co | N4 | O4 | 1.1(3) |
| N1 | Co | N4 | O4 | 136.6(5) |
| N2 | Co | N4 | O4 | 86.6(4) |
| N3 | Co | N4 | O4 | −88.3(4) |
| Co | O5 | C4 | C3 | 8.9(2) |
| Co | O6 | C6 | C5 | 2.2(2) |

Table XII (*Continued*)

| *C. Torsion Angles* | | | | |
|---|---|---|---|---|
| C3 | N1 | C1 | C2 | −79.5(5) |
| C1 | N1 | C3 | C4 | 110.1(5) |
| C5 | N2 | C2 | C1 | −81.5(5) |
| C2 | N2 | C5 | C6 | 97.1(5) |
| N1 | C3 | C4 | O5 | 1.2(2) |
| N2 | C5 | C6 | O6 | 14.5(3) |

Figures 1 through 4 show the asymmetric units of compounds (**I**) through (**IV**), respectively. Their packing diagrams are shown in Figures 5 through 8.

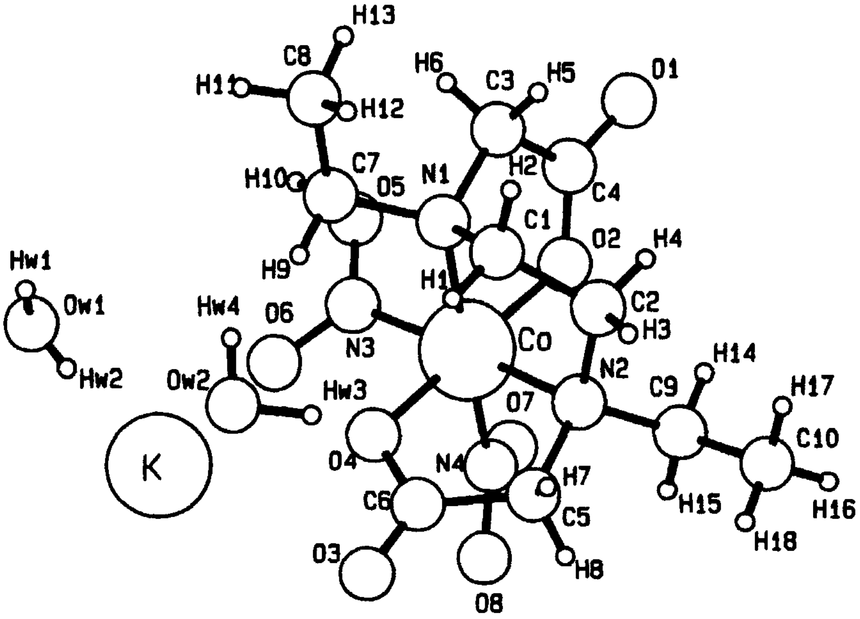

FIGURE 1 The contents of the asymmetric unit in (I). Note that the configuration about Co is Λ while the conformations of O2-C4-C3-N1, N1-C1-C2-N2 and O4-C6-C5-N2 are δ, λ and δ, respectively.

## RESULTS AND DISCUSSION

### Molecular Stereochemistry and Crystallization Mode

Since all four compounds crystallize as racemates, the anions are present in the lattice as Λ and Δ pairs. The enantiomers shown in Figures 1 through 4 are the ones whose coordinates we list and their stereochemistries are, respectively, Λ,

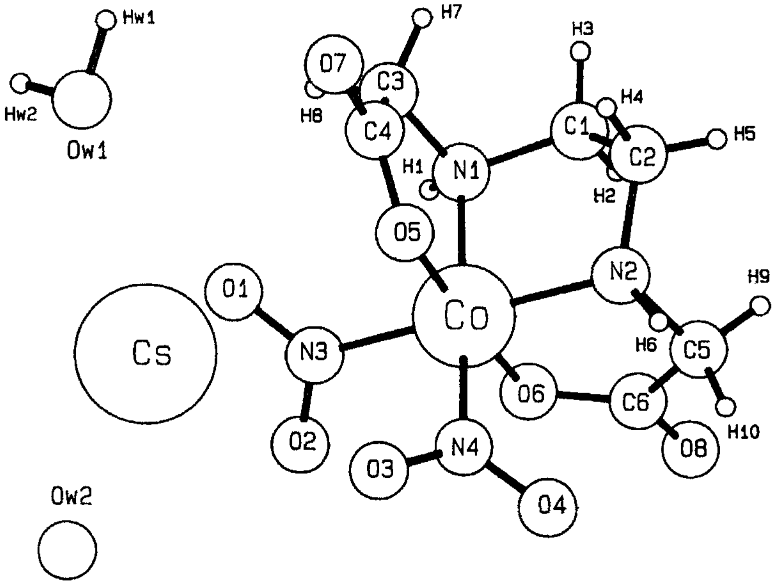

FIGURE 2 The contents of the asymmetric unit in (**II**). Note that the configuration about Co is Δ while the conformations of O2-C3-C4-N1, N1-C1-C2-N2 and O4-C5-C6-N2 are δ, λ and δ, respectively.

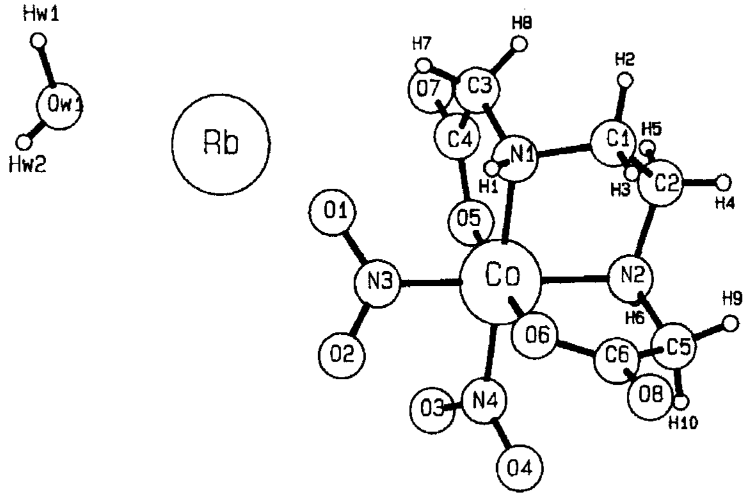

FIGURE 3 The contents of the asymmetric unit in (**III**). The configuration about Co is Λ while the helical chirality of the fragments O5-C4-C3-N1, N1-C1-C2-N2 and O6-C6-C5-N2 are λ, λ and δ, respectively.

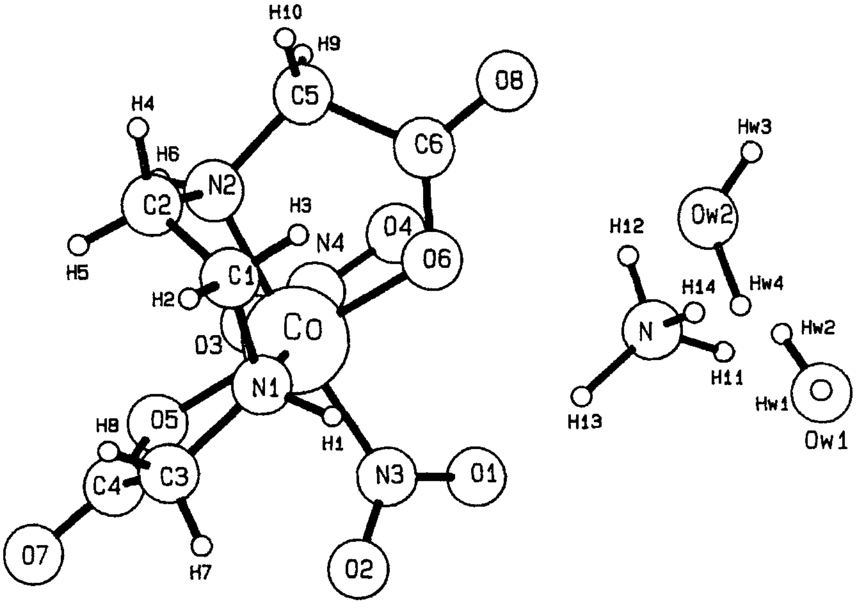

FIGURE 4 The contents of the asymmetric unit in (**IV**). The configuration about Co is Λ while helical chirality of the fragments O5-C4-C3-N1, N1-C1-C2-N2 and O6-C6-C5-N2 are δ, λ and δ, respectively.

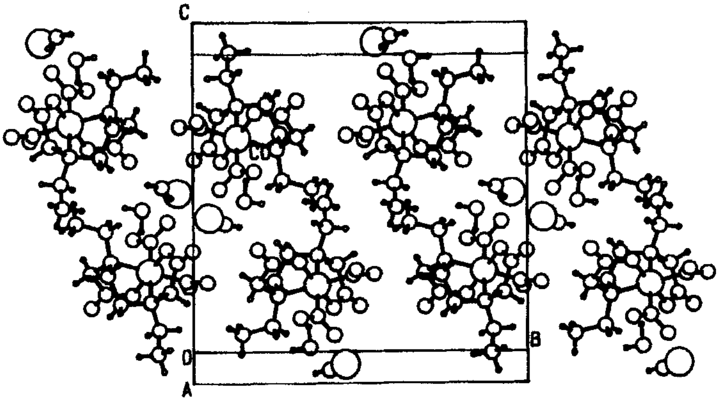

FIGURE 5 The contents of the unit cell in (I). This is an a-projection in which one notes that the alkyl groups are in the center of the cell where they form a hydrophobic cavity, while the hydrophilic-$NO_2$ ligands, potassiums and the waters of crystallization are on the edges of the cell, exposed to the interface between the crystal and the mother liquor. The waters and potassiums link the anions in a sequence (anion)-(water)-(water)-K-(anion).

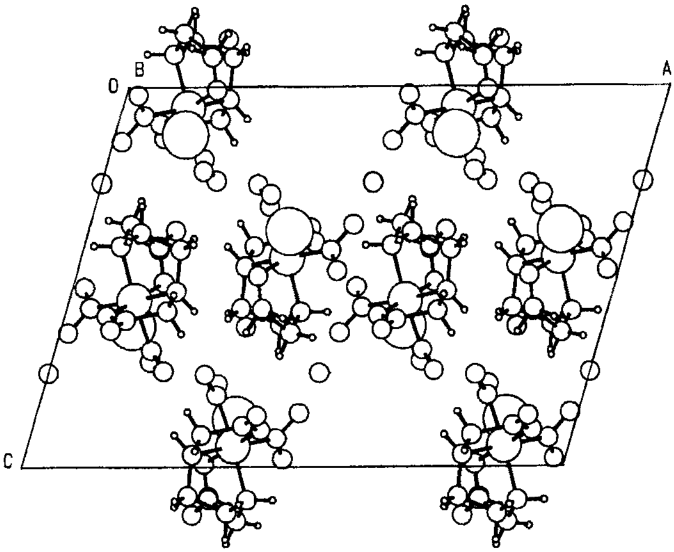

FIGURE 6 The contents of one layer of the unit cell in (**II**). Note the pair of anions at the center of the cell which are realated by the inversion center and which is held together by hydrogen bonds between -$NO_2$ oxygens and -$NH_2$ hydrogens. Note also that the waters link the anions in the a-direction, giving rise to the layer shown (a b-projection) while the potassium ions link layers long the b-direction.

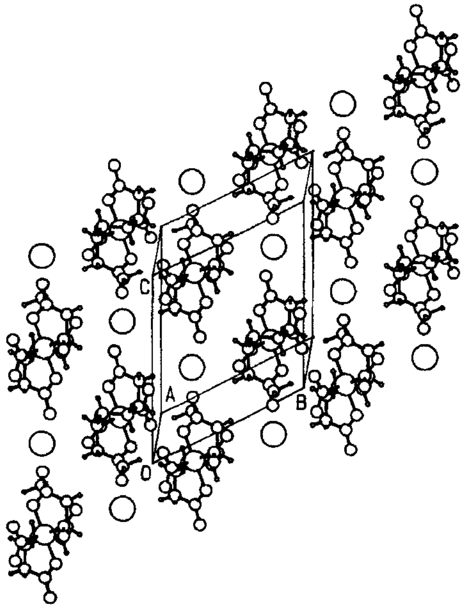

FIGURE 7 The contents of the unit cell in (**III**). Note that, as was the case with (**II**) anion pairs are also formed here (see lower right of cell). The pairs form rows along the bc vector which are linked by the $Rb^+$ cations *via* bonds to the carbonyl and -$NO_2$ oxygens (see Table II).

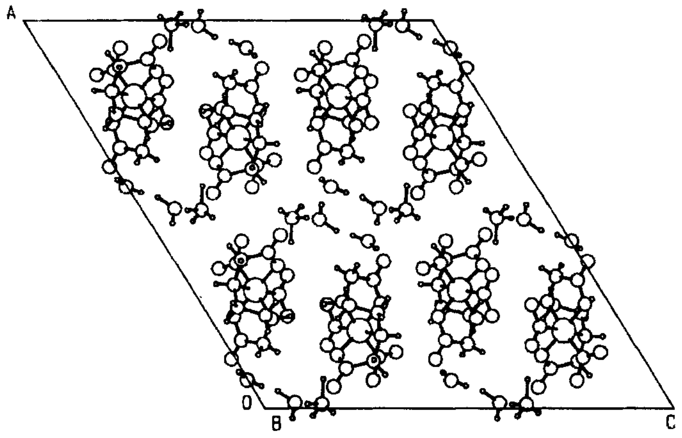

FIGURE 8 The contents of one layer of the unit cell in (IV). Note the cluster of waters and ammonium ions at the center of the cell which two pairs of cations on either side of the inversion center. Each pair hydrogen bonds is linked by hydrogen bonds between -$NO_2$ and carboxylate oxygens as well as by hydrogen bonds between cations, waters and $NH_4^+$ cations as clear from the diagram. Moreover, pairs connected by the inversion center are linked by hydrogen bonded interactions between ajacent waters and $NH_4^+$ cations.

Δ, Λ and Λ. In what follows, the first and third symbols in parentheses refer to the torsional angles of the N-acetato rings and the central one to the diamine ring. Torsional angles for the five-membered rings of (**I**) through (**IV**) are, respectively, 9.1, –53.9, 1.2; –14.1, 52.8, –11.9; –2.8, –52.6, 16.8; 1.2, –52.2, 14.5. In all cases, the diamine nitrogens are asymmetric centers (see Figures 1 through 4) and if one uses the ranking order Co>(en-acetate chain) >acetate chain, the chirality at both, N1 and N2 is R, for compound (**I**). Likewise, using the same ranking system N1 and N2 of (**II**), (**III**) and (**IV**) are, respectively, SS, RR and RR. The stereochemical parameters of the four cations are internally self-consistent and very similar to those described in more detail earlier[1] when we discussed the stereochemistry of (**V**) and (**VI**). Therefore, we refrain from further pursuing this topic here other than to note that, invariably the torsional angle of the acetate chains differ, one always being near zero. Therefore, it is not surprising that in the case of (**III**) the sign of one of the torsional angles of an acetato ring is opposite from that expected. However, the values are so small that forces such as hydrogen bonds and cation O bonded contacts can easily invert the conformation of such rings.

Compound (**I**) crystallizes as a racemate, as we expected in view of the crystallization behavior of the parent, unalkylated compound,[1] which required the presence of hydrogens at the secondary nitrogens in order to form the spiral strings observed in the conglomerate form. Therefore, this result unambiguously supports suggestion (a) above; namely that alkylation would interfere with such string formation, giving rise to a racemate. The presence of two waters of crystallization in (**I**) clouds the issue a little; however, we feel that even in the anhydrous form the crystals will be racemic.

The N,N′-dimethyl derivative also crystallizes as a racemate but the crystals were of poor quality and, thus, we decided it was not worth determining its structure once the main issue was resolved. As for the other three compounds, our results do not completely test suggestion (b) since all three are hydrates, as was the case with (**VI**) which was a racemate. In fact, we note here that the rubidium derivative, (**II**), is not only a monohydrate as was the case with (**VI**), but, in fact, is isomorphous with it. Therefore, we observe consistent behavior between the earlier results with potassium salts and the current ones; and, if we were to properly test suggestion (b) we must do so with their anhydrous crystalline forms. We suspect the anhydrous rubidium salt will be isomorphous with its potassium analogue and, therefore, a conglomerate. This prediction is based on the frequency with which potassium and rubidium salts are isomorphous, as observed here. The cesium coordination demands are so different from those of potassium and rubidium (generally eight or nine as here, and six-coordinate for the potassium and rubidium salts) that we doubt the former will crystallize as a conglomerate isomorphous with the potassium salt. If the cesium salt does crystallize as a conglomerate it will do so in a totally different packing mode from that observed[1] for the potassium salt. The anhydrous rubidium form, if obtainable, will almost certainly be a conglomerate. At the same time, we are surprised at the results we obtained with the ammonium salt (**IV**) since ammonium and potassium salts are also frequently isomorphous; as for example, in the case of alums. Therefore, if an anhydrous ammonium form is obtainable, we suspect it will be a conglomerate, isomorphous with (**V**).

## Packing of the Ions in the Lattices of the Four Compounds

Figure 5 shows the packing of the ions and waters of crystallization in crystals of (**I**) which is typical of the space group $P2_1/n$. Note that the packing consists of islands of four anions held together by bonds with the potassium cations and the waters of crystallization. The inversion center at 1/2, 1/2, 1/2 is obvious and that region shows very clearly the contacts between clusters of anions to be *via* the ethyl chains. Such packing places the hydrophobic alkyl chains on the inside of the crystal and exposes the hydrophilic potassium ions and waters to the interface between the crystal surface and the mother liquor. Note that one water is linked to $-NO_2$ oxygens (Hw3...O5 = 2.05 Å, Hw3...O6 = 2.47 Å) but both bonds of that water are to the same nitrite and there is no water mediated link between anions.

Figure 6 depicts also a typical centrosymmetric structure for (**II**) and the inversion center at 1/2, 1/2, 1/2 is obvious. Note, however, that the cationic, racemic pair thus located has -$NO_2$ oxygens facing -NH hydrogens. Along the *a*-direction, waters of crystallization (located in row along $c$ = 0, 1/2 and 1) link arboxylate oxygens by hydrogen bonds, the shortest of which is 2.06 Å (see Table X). The packing along a, therefore, consists of rows of (racemic pair) -$H_2O$-(racemic pair)-$H_2O$-(racemic pair)-$H_2O$- ... and adjacent rows face each other *via* the aliphatic backbone of the en ring. The layer shown in Figure 6 is linked, above and below by the $Cs^+$ 10 cations which bond six of the eight anionic oxygens, as well as both waters of crystallization. Thus, this packing mode is quite different than the strings found in (**V**) and in (**VI**).

Figure 7 shows the packing mode exhibited by molecules of (**III**) which also pack in pairs, as can readily be observed near the cell origin. In turn, these pairs are linked to one another by (carboxylate–O...Rb) bonds along the *a* direction as shown in Figure 7. Waters of hydration also help link the anionic pairs together. Again, this mode of packing is different than that observed in the cases of (**V**) and (**VI**).

Finally, Figure 8 illustrates the packing in (**IV**) which is a centrosymmetric arrangement, as expected from its space group. Note the way the pairs of waters and an ammonium ion stitch together what can be described as dimeric anions; in turn these dimers are stitched together into tetrameric clusters by the hydrogen-bonded scheme depicted at the center of the cell.

## CONCLUSIONS

As suspected, alkylation of the en nitrogens of (**I**) prevented spiral string formation and led to selection of the racemic crystallization pathway. The other three salts are hydrated and, consistent with the results from (**VI**) also produce racemic lattices. We cannot finish the comparison until anhydrous crystals of the cesium, rubidium and ammonium salts are prepared; however, we feel the latter two have a high chance of crystallizing as conglomerates while the former will either be a racemate or crystallize in space groups other than that for (**V**); that is, it will not be isomorphous with its potassium analogue.

### *Acknowledgments*

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**Supplementary Material Available:** Anisotropic thermal parameters and structure factor tables are available from Ivan Bernal in printed form. the CAD4.DAT; 1 and PSI.DAT; 1 files are also available in PC diskette form, if one is provided with the request.

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