TABLE I

THE HYDROLYSIS CONSTANT FOR THE PERVANADYL REACTION COVERING THE RANGE IN FREE HYDROGEN ION CONCENTRATION OF 0.2×10^{-3} TO 20×10^{-3} M AT AN IONIC STRENGTH OF 3.0 AND 25°

Concn., M	Wave length, $m\mu$	Log K
1.05×10^{-3}	410	-5.8
1.05×10^{-3}	400	-5.8
1.05×10^{-3}	390	-5.8
1.05×10^{-3}	380	-5.9
5.25×10^{-4}	320	-5.7
5.25×10^{-4}	310	-5.5
5.25×10^{-4}	300	-5.6
5.25×10^{-4}	290	-5.6
1.05×10^{-4}	270	-6.0
1.05×10^{-4}	260	-5.9
1.05×10^{-4}	250	-6.0
1.05×10^{-4}	240	-6.1

Av. -5.8 ± 0.18

Procedure.—Aliquots of a solution containing the vanadium concentration under investigation were mixed with aliquots of a 3.0 M perchloric acid solution containing the same vanadium concentration. To attain equilibrium the mixed solutions were brought to a quick boil and cooled to 25°.[11] It was found that irreproducible results were obtained if the temperature of the solutions were only brought to 70–80°. The establishment of equilibrium was ascertained by observing that the absorbance and pH values measured on the day of mixing were identical with those measured after three days. The three vanadium concentrations investigated were 1.05×10^{-4} M, 5.25×10^{-4} M and 1.05×10^{-3} M. Typical results are presented in Fig. 1.

The free hydrogen ion concentration was determined from pH measurements utilizing a calibration procedure similar to that previously described.[18] In this case the electrodes were calibrated by obtaining pH values of acid solutions between 0.2×10^{-3} M to 20×10^{-3} M. As in the previous publication, the ionic strength was maintained at 3.0.

Typical straight line plots obtained upon application of equation 6 are presented in Fig. 2. The calculated values of the logarithm of the hydrolysis constant for twelve wave lengths, a tenfold change in vanadium concentration and a hundred-fold change in hydrogen ion concentration are summarized in Table I. The logarithm of the molar extinction coefficients are plotted *versus* wave length in Fig. 3.

Discussion

The value of -5.8 ± 0.18 obtained for the logarithm of the hydrolysis constant is in excellent agreement with the value of -5.5 ± 0.15 obtained by Rossotti and Rossotti at an ionic strength of 3.0. By utilizing the spectrophotometric method, the experimental data for this reaction have been extended from an eightfold change in vanadium concentration to a two hundred-fold change.

While our data fit the decavanadate mechanism very well, they are not sufficiently unique to distinguish between a decavanadate and hexavanadate mechanism. However, the data of Rossotti and Rossotti distinguish between these two mechanisms. This fact combined with the accompanying agreement of the hydrolysis constant over a wide range in vanadium concentration strongly supports the decavanadate mechanism for the hydrolysis of the pervanadyl ion.

UPTON, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structures of Ammonium and Rubidium Ethylenediaminetetraacetatocobaltate(III)[1]

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Isomorphous crystals of $NH_4CoY \cdot 2H_2O$ and $RbCoY \cdot 2H_2O$ ($Y^{4-} \equiv$ ethylenediaminetetraacetate) have a four-molecule orthorhombic cell of space group $P2_12_12_1$. The techniques of isomorphous replacement, Fourier and difference syntheses were applied to spectrometrically measured X-ray zonal data from single crystals to achieve determination of structure. The sexadentate octahedral complex CoY^- (Fig. 2), containing five chelate rings, shows effectively twofold symmetry about an axis bisecting the NCoN angle of the ethylenediamine (E) ring. The four glycinic rings are thus classified into pairs: the relatively flat and unstrained R rings lie in planes nearly at right angles to each other and to E; the strongly folded and quite strained G rings, together with E, form closing Co–O, Co–N bonds in a girdle around the central atom.

Introduction

The capacity of ethylenediaminetetraacetic acid (abbreviated formula, H_4Y) to complex with many different cations has been studied by many workers. Among crystalline complexes of the transition elements first prepared by Brintzinger, et al.,[3] was the diamagnetic[4] $NaCoY \cdot 4H_2O$. Since the complexing species contains six functional groups, a sexadentate complex CoY^- with five five-membered chelate rings is theoretically possible. The existence of the sexadentate CoY^- and also of the quinquedentate $CoYX^=$, $X^- = Cl^-$, Br^-, NO_2^-, receives strong support from the physico-

chemical studies of Schwarzenbach[5] and the infrared studies of Busch and Bailar[6] and Morris and Busch.[7] The X-ray study now reported was undertaken to determine directly the configuration and bond data for one of the stable complexes, namely, CoY^-. Orthorhombic crystals of NH_4-$CoY \cdot 2H_2O$ and $RbCoY \cdot 2H_2O$ prove to be isomorphous and well suited to structure determination.

Experimental

Crystals of $NaCoY \cdot 4H_2O$, $NH_4CoY \cdot 2H_2O$ and $RbCoY \cdot 2H_2O$ were prepared by methods similar to those used by Burke.[8] A slurry containing newly precipitated $Co(OH)_2$

(1) Supported by National Science Foundation.

(2) General Electric Company Fellow, 1956–1957.

(3) H. Brintzinger, H. Thiele and U. Müller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943).

(4) W. Klemm, *ibid.*, **252**, 225 (1944).

(5) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

(6) D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **75**, 4574 (1953).

(7) M. L. Morris and D. H. Busch, *ibid.*, **78**, 5178 (1956).

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and an equimolar quantity of solid H_4Y was warmed to give a solution red-violet in color. Ammonia, rubidium carbonate or sodium hydroxide was added in equivalent amount to give a neutral solution. The CoY^- ion was then oxidized to CoY^- by slowly adding an excess of a 3% solution of hydrogen peroxide to the warm solution. Following concentration by further heating, the deep purple solution was filtered and put aside until crystallization occurred. Crystallization from aqueous solution and from methanol–water mixtures afforded crystals of identical diffraction patterns.

Purple crystals of $NH_4CoY \cdot 2H_2O$ and $RbCoY \cdot 2H_2O$ grew as flat needles of hexagonal cross-section with good lateral face development but with broken or irregular ends. Crystals up to 10 mm. in length (along the short a translation of the unit cell), but rarely more than 0.3 mm. thick were obtained. Microscopic examination, when correlated with the axial assignment given by the X-ray data, gave the following results.

Crystals of both compounds exhibit parallel extinction between crossed nicols and are biaxial negative. The acute bisectrix lies along a and the optic axes lie in (001). Refractive indices of $NH_4CoY \cdot 2H_2O$, as determined by the immersion method,[9] are $\alpha = 1.586, \beta = 1.617, \gamma = 1.625$. The calculated optic axial angle is 114°. The orientation of the indicatrix is α, β, γ, respectively, parallel to a, c, b of the crystal.

Determination of the lattice constants and the probable space groups for all three compounds utilized extensive data from oscillation and Weissenberg equi-inclination photographs taken with Cu $K\alpha$, Mo $K\alpha$ and Co $K\alpha$ radiations, this last to avoid the strong fluorescence of cobalt in the crystal when the more usual copper radiation was employed. All three compounds displayed the diffraction symmetry, mmm. The extinctions[10] given by $NH_4CoY \cdot 2H_2O$ and $RbCoY \cdot 2H_2O$ are those uniquely characterizing the space group $P2_12_12_1$, by $NaCoY \cdot 4H_2O$ those demanded by $Pna2_1$ and $Pnam$; this latter space group is eliminated by our observation of pyroelectricity in the sodium compound. With four molecules per unit cell in every case, we obtain the cell data of Table I.

TABLE I

UNIT CELL DATA

| Compound | Lattice constants, Å.[a] | | | Density, g./cc. | |
	a	b	c	Calcd.	Expt.[b]
$NH_4CoY \cdot 2H_2O$	6.46	23.16	10.09	1.765	1.75
$RbCoY \cdot 2H_2O$	6.43	23.08	10.18	2.06	2.07
$NaCoY \cdot 4H_2O$	6.50	19.1	13.6	1.74	1.75

[a] Values for $NH_4CoY \cdot 2H_2O$ and $RbCoY \cdot 2H_2O$ accurate to 0.2%, for $NaCoY \cdot 4H_2O$ to about 0.5%. [b] By flotation method.

At this stage the advantages of dealing with the isomorphous rubidium and ammonium salts were so manifest that study of the sodium compound was discontinued. Using the technique described earlier[11] (but using a proportional rather than a Geiger counter), integrated intensities for the three principal zones of $NH_4CoY \cdot 2H_2O$ and for the $0kl$ and $hk0$ zones of $RbCoY \cdot 2H_2O$ were measured on a G.E. XRD-3 spectrometer modified for single crystal work. Specimens were generally cut and ground to cylindrical form along the appropriate axes. Radii of the specimens of the rubidium compound were 0.090 and 0.095 mm.; radii of all specimens of the ammonium compound were $\lesssim$ 0.09 mm. With use of Mo $K\alpha$ radiation for all spectrometric measurements, no corrections for variation of absorption with scattering angle were required. The intensity data were converted to relative $|F|^2$ values in the usual manner. A scaling factor to put the $|F|^2$ data on an absolute basis together with an averaged isotropic thermal parameter were determined for each zone of both compounds by the Wilson[12] method. Values of these parameters were subject to moderate alteration during the later stages of refinement by difference syntheses[13];

throughout the analysis, however, values of the thermal parameter B were confined to the range 2.1–2.6 Å.[2] Measurable reflections were practically confined to the range sin θ/λ <0.66 for $NH_4CoY \cdot 2H_2O$, sin θ/λ <0.75 for $RbCoY \cdot 2H_2O$. Within the range noted for $NH_4CoY \cdot 2H_2O$, 441 of a theoretical total of 591 forms were recorded.

Polarimetric Data.—The space group $P2_12_12_1$ requires that the four complex anions of the unit cell all be congruent. If the anions are optically active, there must be complete sorting during crystallization, i.e., each single crystal must contain only d- or only l-isomers. A crystal of $RbCoY \cdot 2H_2O$ weighing 0.28 mg. was dissolved in 1.0 ml. of water and the optical rotation of the solution measured in a polarimeter. Specific rotations of $[\alpha]^{25}_{5461}$ $-1600°$ and $[\alpha]^{25}$D $+310°$ resulted. A second determination, for which a crystal of $NH_4CoY \cdot 2H_2O$ weighing 0.61 mg. was dissolved in 2.8 ml. of water gave $[\alpha]^{25}_{5461}$ $+1510°$; it is evident that one crystal containing d-isomers and the other l-isomers were picked by chance. For a solution of d-$KCoY \cdot 2H_2O$ which had been resolved by chemical means, Dwyer,[14] et al., report $[\alpha]^{20}_{5461}$ $+1000°$, $[\alpha]^{20}$D $-150°$. In view of the small rotation and the possibility of substantial error in weighing the single crystals, we cannot claim high accuracy for our results.

Determination of Structure

The space group $P2_12_12_1$ provides only fourfold general positions[10]: the asymmetric unit is one stoichiometric molecule and the structure has 72 coördinates to be determined, exclusive of hydrogen positions. However, the short a translation suggests (correctly) that the structure is only one complex thick in this direction.

As soon as the intensity data for the $0kl$ and $hk0$ zones of $NH_4CoY \cdot 2H_2O$ became available, we applied the heavy atom technique[13] to the analysis of the Patterson syntheses[13] $P(Y,Z)$ and $P(X,Y)$ and were able to deduce positions for cobalt atoms not far from those established for the final structure. While pretty well convinced that we had a sufficient basis from which to develop the structure through the usual cycles of successive approximation, we had meanwhile established the isomorphic character of the ammonium and rubidium compounds. Analysis of $P(X,Y)$ and $P(Y,Z)$ for $RbCoY \cdot 2H_2O$ gave positions for both rubidium and cobalt atoms, coördinates for the latter agreeing well with those found earlier for the ammonium salt. By assuming that the two crystals differed essentially only in the scattering of the univalent cation, NH_4^+ or Rb^+, i.e., by applying the method of isomorphous replacement,[13,15] we were enabled to determine the signs of 116 $0kl$ structure factors, some 54% of the total number recorded for the ammonium compound. Of the 116 phases, 68 were of the same sign as given by our limited application of the heavy atom method, two were of opposite sign, and the remaining 46 had been previously undetermined.

Using the amplitudes of known sign for $NH_4CoY \cdot 2H_2O$, the incomplete Fourier synthesis $\rho(y,z)$ was computed. The projection showed 17 peaks in addition to that of cobalt. By assigning a scattering power[16] equal to that of nitrogen to each of these 17 peaks we were able to assign further phases through calculation of structure factors[17] and hence add terms to $\rho(y,z)$. After two cycles of structure factor calculation, the sign of only one observed amplitude remained undetermined and $\rho(y,z)$ was in essentially the final form of Fig. 1.

During the refinement of $\rho(y,z)$ it became possible to interpret the projection in terms of the sexadentate octahedral model for the complex anion of Fig. 2. Although the orientation of the complex with respect to a is favorable to maximum resolution in projection, some overlapping (Fig. 1) is inevitable; note that one carbon and one oxygen atom are exactly superposed. The integrated electron density of the overlapped peaks is in good agreement with the interpretation. The bond framework, as sketched in Fig. 1 for the

(9) C. W. Bunn, "Chemical Crystallography," Oxford University Press, London, 1946.

(10) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

(11) J. L. Hoard, R. E. Hughes and D. E. Sands, THIS JOURNAL, 80, 4507 (1958).

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(13) Cf., H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons, Ltd., London, 1953.
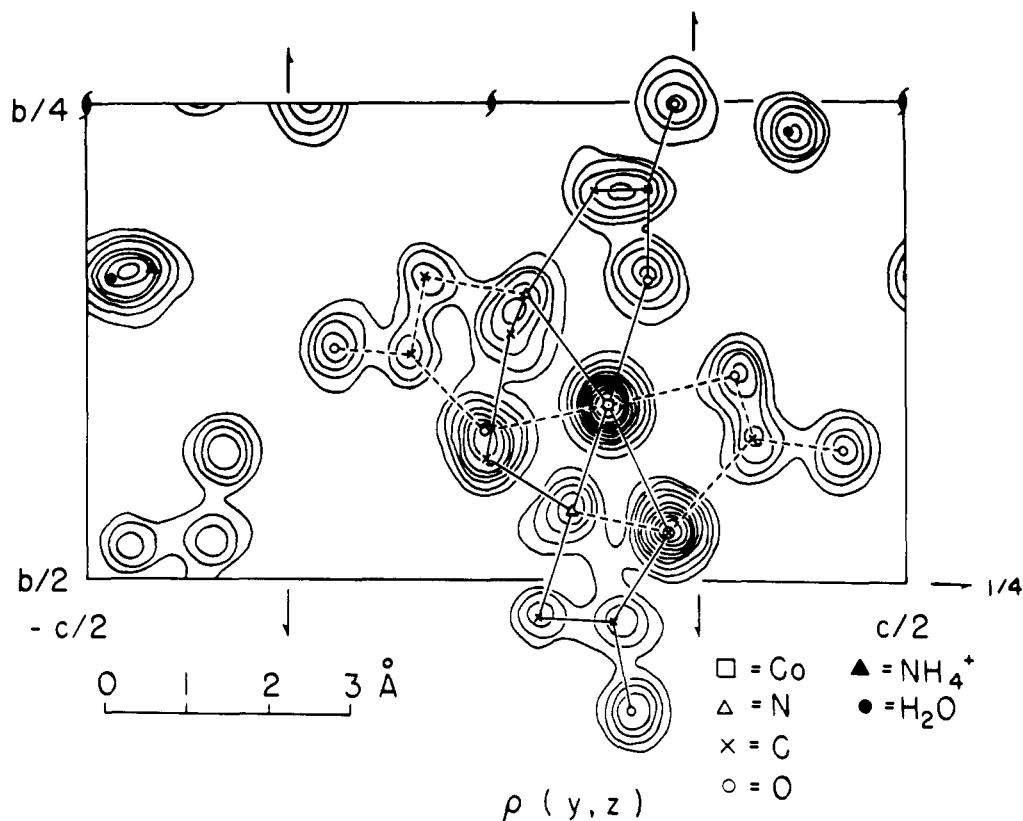
(14) F. P. Dwyer, E. C. Gyarfas and D. P. Mellor, J. Phys. Chem., 59, 296 (1955).

(15) J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953.

(16) The atomic form factors of J. Berghius, I. M. Haanapel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, Acta Cryst., 8, 478 (1955), were used for light atoms and for Rb^{+}. The form factor used in the last stages of computation for cobalt was that of L. H. Thomas and K. Umeda, J. Chem. Phys., 26, 293 (1957).

(17) Calculations performed on the IBM 650 computer using a program written for use with the Floating-Decimal Interpretive System.

Fig. 1.—Electron density in $NH_4CoY\cdot2H_2O$ projected onto (100). Contours at intervals of $2e/Å.^2$ starting with $4e/Å.^2$ contour except around Co where the interval is $5e/Å.^2$ starting with $5e/Å.^2$ contour. The skeleton of one complex anion is indicated.

complex, connects final atomic positions as provided by further refinement (*vide infra*) through difference syntheses.[13] Figure 3 shows for comparison the electron density map $\rho(y,z)$ for $RbCoY\cdot2H_2O$. The close similarity of the two projections, apart from substitution of the heavy rubidium peak for that of ammonium ion, commands confidence in the analysis. The quite minor differences which appear between the two structures are discussed later.

Analysis of the $hk0$ data, leading to electron density maps $\rho(x,y)$ for both crystals, paralleled that of the $0kl$ data, and need not be presented in detail. As the x-coördinates of both cobalt and rubidium or ammonium were not far from ±0.25, the determination of phase was especially easy for reflections having $h + k$ even, correspondingly difficult for $h + k$ odd. However, amplitudes in the latter class could be added with confidence a few at a time in progressive cycles of computation until $\rho(x,y)$ was complete (see Fig. 4 for $\rho(x,y)$ of $NH_4CoY\cdot2H_2O$). The (001) projections for the two crystals were in excellent agreement with each other and with the (100) projections, and the essential character of the structure was no longer in doubt. Simultaneous study of Figs. 1–4 makes clear the detailed interpretation of the electron density maps.

Further refinement of the structure utilized difference syntheses,[13] $\rho-\rho c$, ρ and ρc being, respectively, the projected electron densities for observed and calculated Fourier coefficients. Refinements of the $0kl$ and $hk0$ data were carried along concurrently for each crystal but were carried further to a more satisfactory conclusion for $NH_4CoY\cdot2H_2O$; the data for the ammonium compound were intrinsically better suited to our primary objective, namely, to get an accurate description of the complex anion. The scale factor and the isotropic thermal parameter for each set of zonal data were re-evaluated during successive cycles of computation[18] by the usual least squares fitting of a plot of log $([Fc]/[F])$ vs. $(sin\ \theta/\lambda)^2$.

(18) Carried out on the IBM computer using a Fourier series program kindly supplied by Miss Dorothy Booth of the Bell Telephone Laboratories.
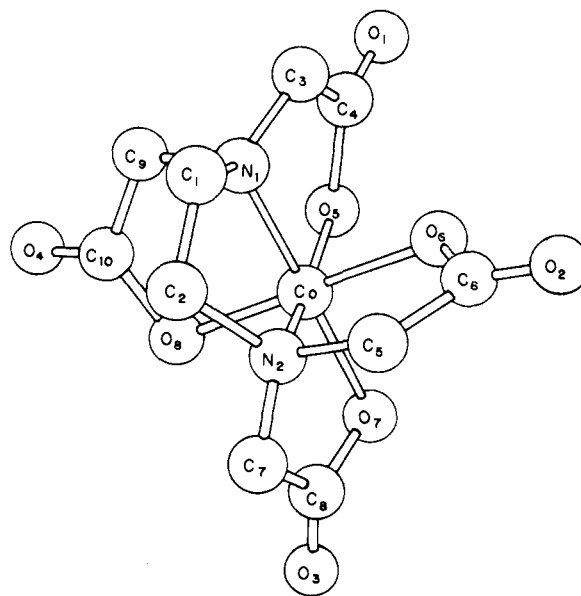

Fig. 2.—Model in true perspective of CoY^-, only slightly tilted from the orientation in Fig. 1.

The cycle of refinement was continued for the ammonium compound until nearly all atomic centers were in regions of zero slope on the difference maps. Moderately negative areas around some atomic centers, particularly those of oxygen atoms not bonded to cobalt, indicated that slightly larger values of B should be assigned to these atoms. This was not done since we judged the gain in accuracy would be small. The occasional indications of reasonable hydrogen positions
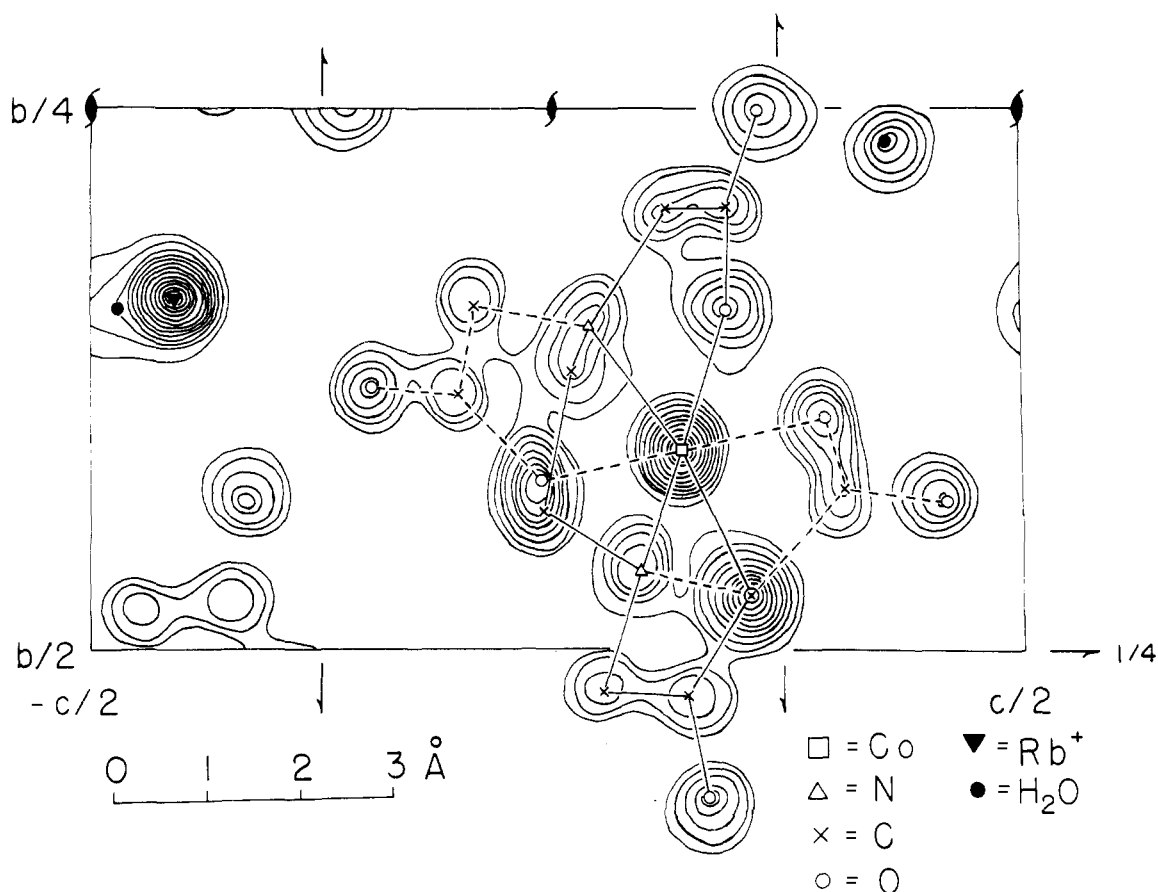
Fig. 3.—Electron density in RbCoY·2H₂O projected onto (100). Contours around Rb⁺ at intervals of 5e/Å.² starting with 10e/Å.² contour; otherwise as in Fig. 1. The indicated atomic positions in the complex are those of the ammonium salt.

given by the difference maps also were ignored: we could not go further with a single thermal parameter, and we could see no objective method for handling overlapping with several (up to 48/projection) different B's treated as disposable parameters.

Following refinement by difference syntheses of the $0kl$ and $hk0$ data from NH₄CoY·2H₂O, it was realized that the (x,z)-coördinates of the oxygen atom O_{II} of a water molecule were still relatively uncertain because of strong overlap on both projections. It was also seen that this atom should be one of only three or four which ought to be clearly resolved on the (010) projection. Intensities of $h0l$ reflections were measured, $\rho(x,z)$ was found to agree with expectation, and the data were refined by difference syntheses. The agreement with the earlier results was highly satisfactory, and definitely improved (x,z)-coördinates were obtained for O_{II} and NH₄⁺.

Final values of B obtained for the three zones of NH₄-CoY·2H₂O were 2.14 ± 0.03 Å², for the two zones of Rb-CoY·2H₂O, 2.5 Å². (The difference maps for the rubidium compound indicated indeed that Rb⁺ should be assigned a larger than average thermal parameter, but the corresponding further refinement was not attempted. It will be seen that NH₄⁺, unlike Rb⁺, is tied into a hydrogen bonded network.) Positional coördinates from well resolved peaks were weighted heavily in determining the final values (Table II), the selection process being expedited by the generally good agreement from various zones. The agreement between observed (F) amplitudes and those calculated (F_c) on the basis of the final parameter values was generally very satisfactory,[19] there being no outstanding discrepancies for

(19) Following submission with the manuscript for examination by referees, amplitude data for NH₄CoY·2H₂O have been submitted as Document number 5745 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in ad-

either compound. Grinding of the specimens may have been partly responsible for the apparent absence of appreciable extinction.

TABLE II

ATOMIC COÖRDINATES IN NH₄CoY·2H₂O[a]

Atom	10^3x	10^4y	10^4z	Atom	10^3x	10^4y	10^4z
Co	275	4087	1401	C₉	321	3424	− 855
NH₄	764	3365	−4218	C₁₀	139	3828	−1040
N₁	424	3510	420	O₁	116	2510	2231
N₂	482	4650	940	O₂	655	4310	4236
C₁	638	3726	182	O₃	89	5672	1666
C₂	617	4376	− 86	O₄	19	3797	−1967
C₃	411	2980	1262	O₅	102	3448	1902
C₄	196	2962	1880	O₆	426	3924	2968
C₅	610	4744	2140	O₇	139	4745	2145
C₆	574	4273	3159	O₈	119	4230	− 125
C₇	370	5199	560	O₁	743	2659	3643
C₈	181	5227	1489	O₁₁	236	3428	−4726

^{a} (1) xCo is more accurately 0.2748. (2) Rounding off of y and z values for light atoms to the nearest 0.0002 and 0.0005, respectively, is in order. (3) In RbCoY·2H₂O we find for Rb⁺: $x = 0.7475$, $y = 0.3402$, $z = -0.4099$; for Co: $x = 0.2638$, $y = 0.4092$, $z = 0.1339$. A complete list of atomic coördinates may be obtained from the authors.

A further idea of the consistency of the analysis is given by the values of $R = \Sigma \mid \mid F \mid - \mid F_c \mid \mid /\Sigma \mid F \mid$, computed in two different ways for each set of zonal data. When all unobserved reflections in the range sin θ/λ <0.66 are included at half their minimum observable values, $R = 0.150 \pm$

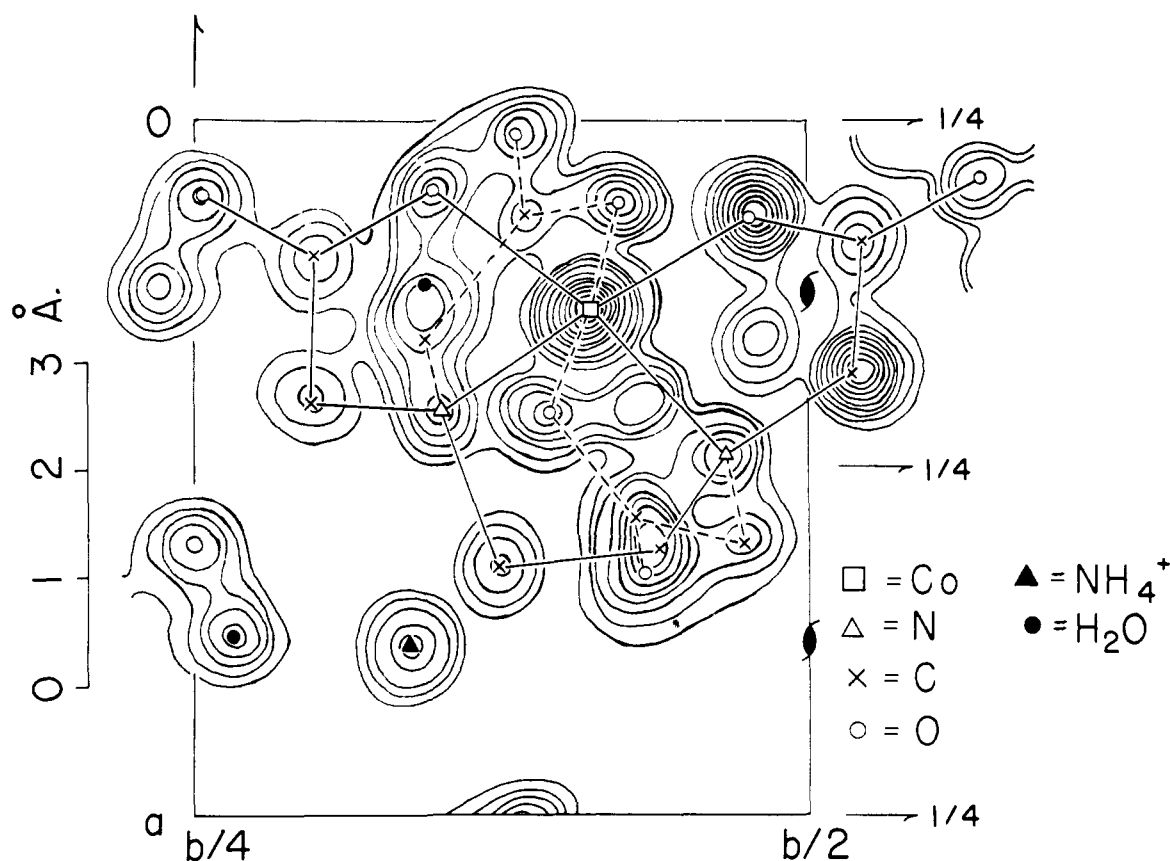vance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

Fig. 4.—Electron density in NH₄CoY·2H₂O projected onto (010). Contours as in Fig. 1. The skeleton of one complex anion is indicated.

0.005 brackets the results for the three zones of NH₄CoY·2H₂O. When unobserved reflections are ignored, $R = 0.14$, 0.14, 0.11, the low figure doubtless arising[20] from the substantially larger proportion of unrecorded reflections in the corresponding zone. Values of 0.15, 0.18 were calculated on the first basis for RbCoY·2H₂O.

Discussion of Results

The cobalt atom of the complex anion (Fig. 2) is bonded octahedrally to the two nitrogen atoms and one oxygen atom from each of the four carboxylate arms of the complexing species. The plane defined by nitrogen and the central atoms is designated NNM. The oxygen atoms O_5 and O_7, opposite, respectively, to N_2 and N_1 (Fig. 2), are each 0.20° Å. from, but on opposite sides of NNM. Speaking roughly, three of the five chelate rings form a girdle about cobalt, being closed in or near NNM through bonds to N_1, N_2, O_5, O_7. Unlike these rings, the remaining two are virtually flat; they lie in planes nearly perpendicular to each other and to NNM, with Co–O_6 and Co–O_8 bonds approximately along the normal to NNM. A line in NNM which, within experimental error, bisects the opposite angles N_1CoN_2 and O_5CoO_7 (Fig. 2) and also passes nearly through the midpoint of the C_1–C_2 bond, serves effectively as an axis of twofold symmetry for the entire complex. This *quasi*-twofold axis classifies the five rings into three groups: E, the ethylenediamine ring, $CoN_1C_1C_2$-N_2Co; G, the glycinic rings, $CoN_1C_3C_4O_5Co$ and

$CoN_2C_7C_8O_7Co$; R, also glycinic rings, $CoN_1C_9C_{10}$-O_8Co and $CoN_2C_5C_6O_6Co$ (Fig. 2). G and R will be seen to differ substantially as regards bond angles.

The data provide from two to six independently determined values of the bond length for each of the following classes of bonds: Co–N(2); Co–O(4); C–N(6); C–C(5); C–O(ring, 4); C=O (external, 4). In NH₄CoY·2H₂O the mean bond length with mean deviation and (in parentheses) maximum deviation from the mean for each class are (all values in ångström units)

Co–N, 1.925 ± 0.005 (0.005); C–C, 1.53 ± 0.01 (0.01); C–N, 1.49 ± 0.01 (0.02); Co–O, 1.900 ± 0.015 (0.030); C–O, 1.30 ± 0.02 (0.03); C=O, 1.22 ± 0.01 (0.01)

Standard deviations in bond lengths as estimated by Cruickshank's procedure[21] are: Co–N or Co–O, 0.011 Å.; C–O, 0.018 Å.; C–N, 0.019 Å.; C–C, 0.021 Å. Only for Co–O is the maximum deviation from the mean sufficiently larger than the standard deviation to suggest[21] possible significance. Division into two groups corresponding to the *quasi*-twofold axis gives Co–O_G, 1.915 ± 0.005 Å. and Co–O_R, 1.885 ± 0.015 Å. The comparison gives a possibly significant difference (0.030 Å.), though weakened by the observed variation in the two Co–O_G lengths. Bond lengths from Pauling's Tables[22] are 1.88 Å. for Co–O, 1.92 Å. for Co–N.

(20) Cf. D. L. Coursen and J. L. Hoard, THIS JOURNAL, **74**, 1742 (1952).

(21) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949); F. R. Ahmed and D. W. J. Cruickshank, *ibid.*, **6**, 385 (1953).

(22) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

Our results, 1.53 Å. for C–C, 1.49 Å. for C–N, compare satisfactorily with 1.54 and 1.47 Å., expected[15] values for these bonds from earlier structural data. The difference between the chelate ring C–O distance, 1.30 Å., and the external C=O distance, 1.22 Å., is significant. Notwithstanding the additional bond formed by oxygen with cobalt, the ring C–O value comes out substantially smaller than expected[15] (ca. 1.42 Å.) for a standard single bond. The external carbon–oxygen bond is little if at all longer than corresponds to a standard double bond.

Averaged bond lengths from the less accurate RbCoY·2H₂O data are Co–N, 1.93 ± 0.01 Å., Co–O_G, 1.915 ± 0.015 Å., Co–O_R, 1.895 ± 0.015 Å., C–C, 1.54 Å., C–N, 1.48 Å., C–O, 1.29 Å., C=O, 1.19 Å., in generally good agreement with the NH₄CoY·2H₂O results. For the sake of brevity, our further discussion of the configuration of the complex anion will present only data for the ammonium compound.

The individual bond angles (excepting the unique N_1CoN_2 and O_5CoO_7) are associated in pairs by the *quasi*-twofold axis. In only three or four instances are the departures of the real structure from the averaged structure corresponding to a twofold axis large enough to attain possible significance in terms of statistical criteria,[21] notably for the NCC angles of the E ring. (The methylene carbon atoms of E are involved in considerable overlap on the projections.) In any event it would seem that the averaged model best represents the complex of greatest chemical interest, and its use simplifies and clarifies presentation of our most interesting structural results.[23] For each bond angle type we list the mean value and deviation from the mean; for each ring type we give also the sum of bond angles ($\leq 540°$). Typical values of the appropriate standard deviations[21] are: CoNC and CoOC, 0.75°; NCC and OCC, 1.1°; NCoN and NCoO, 0.60–0.65°.

R: CoNC, 108.1 ± 1.2°; NCC, 111.1 ± 0.1°; CCO, 116.9 ± 1.1°; COCo, 113.1 ± 0.4°; NCoO, 88.55 ± 0.25; sum, 537.75 ± 0.05°

G: CoNC, 105.9 ± 1.4°; NCC, 106.4 ± 1.3°; CCO, 115.1 ± 0.7°; COCo, 112.9 ± 0.5°; NCoO, 83.2 ± 0.4°; sum, 523.5 ± 0.2°

E: CoNC, 107.5 ± 0.8°; NCC, 108.1 ± 2.1°; NCoN, 89.7°; sum, 520.9°

Between rings: O_GCoO_G, 104.0°; O_GCoO_R, 93.1 ± 0.8°, 86.0 ± 0.3°; O_RCoN, 92.5 ± 0.7°; C_ENC_G, 116.1 ± 1.5°; C_ENC_R, 108.6 ± 0.8°; C_GNC_R, 110.4 ± 0.3°

>C=O: CCO, 121.4 ± 0.3° (G), 121.3 ± 1.8° (R); OCO, 123.2 ± 0.3° (G), 121.7 ± 1.1° (R)

We note first that just one of the four C·COO groups shows an apparently significant departure from planarity: C₆ is calculated to lie 0.10 Å. out of the plane C₅O₂O₆ defined by the three atoms attached to C₆ (Fig. 2).

The sums of the ring bond angles show that only the R rings approach closely to planarity. The sum of the ideal angles for E, 4(109.5) + 90, is 528° as compared with 521° in the present instance.

(23) Tables of individual bond lengths and angles are available in the Ph.D. Thesis of H. A. Weakliem, Jr., "The Crystal Structures of Ammonium and Rubidium Ethylenediaminetetraacetatocobaltate (III)," Cornell University Library, Ithaca, N. Y., 1958.

The configuration of E in the averaged model corresponds approximately to a rotation of the C–C bond about the twofold axis to place the carbon atoms on opposite sides and equidistant (0.29 Å.) from NNM. Although we are uncertain as to what values are "ideal" for bond angles at carboxylate carbon and oxygen when chelation to Co(III) occurs, the available evidence suggests that unstrained glycinic rings of this type should be nearly or exactly planar; in any event, this conclusion seems to arise from the further consideration of our data.

The description of the averaged complex of twofold symmetry is greatly clarified by specifying the departures from an initially oversimplified configuration. We first suppose that two flat R rings are present in planes mutually perpendicular to each other and to NNM, this being permitted if (1) the E ring is opened, let us say, between the carbon atoms and (2) G rings are not yet closed. Assuming regular tetrahedral bond angles at nitrogen, the C_E and C_G atoms bonded to each nitrogen (e.g., C₂, C₇ to N₂ in Fig. 2) are both 0.70 Å. from NNM on the side opposite to an R ring; further, the two C_E (C₁, C₂) atoms across NNM from each other are too far apart for closure of E. Bonding of these atoms becomes possible through rotation of the nitrogen bond systems, each about 15°, around the Co–N bonds, accompanied, as explained later, by some adjustments in bond angles at nitrogen; the C_E atoms are then 1.53 Å. apart and each is 0.29 Å. from NNM. The bulge (0.35 Å. maximum at methylene carbon) introduced into an R ring by the rotation is partially smoothed out by small angular adjustments, e.g., the angle NCoO_R between E and R opens up 2–3° as R attempts to follow the rotation as a unit. The departures in the averaged model of nitrogen and cobalt atoms from the reference plane of the C·COO group are estimated, respectively, as 0.3 and ≤ 0.2 Å. in the same sense.

The rotations of the bond systems at nitrogen atoms which allow closure of E further displace the methylene carbon atoms C_G (C₇, C₃) attached to nitrogen until each is about 1.0 Å. from NNM, yet, ideally, the Co–O_G bonds closing G rings should lie in NNM. Closure of a G ring is then attained: (1) by spreading significantly (to 116°) the C_ENC_G angle between E and G; (2) by accepting significantly smaller values than ideal for ring bond angles at cobalt, at nitrogen and probably at carbon (every bond angle in G is formally calculated as smaller than the corresponding value in R); (3) by allowing the closing Co–O_G bond to angle away some 6° from NNM so that all of the ring excepting the Co–N bond lies to one side of this plane. We note also the very open 104.0° angle O_GCoO_G between G rings. The distortion of G from planarity consists of a major folding away from NNM about an axis through nitrogen and (ring) oxygen atoms plus a smaller reversed folding about an axis through the same oxygen and methylene carbon. Nitrogen and cobalt atoms in G lie on opposite sides of the C·COO reference plane, itself inclined about 30° to NNM.

Some distortion from the averaged model of two-

fold symmetry is established for the anion as packed within the crystal. The rotations about Co–N bonds of the C–N bond systems at nitrogen are unequal, being about 10° larger at N_2 than at N_1. Comparison of the R rings containing, respectively, N_1, O_8 and N_2, O_6, might then show evidence of greater strain in the latter; indeed, the Co–O_6 bond is apparently longer (in the RbCoY·2H$_2$O data also) by a possibly significant 0.03 Å. We must note, however, that O_6 is hydrogen bonded to a water molecule (vide infra), the only ring oxygen atom to be thus involved. Other than this one case, we find no apparently significant indications of differing strains either within the R pair or within the G pair of rings. The further discussion returns to the simpler case of the averaged model of twofold symmetry.

We note that difficulties of ring closure are almost wholly associated with formation of the girdle consisting of E and two G rings. It appears, moreover, that the presence of R rings is probably favorable to the coexistence of G rings, by coöperating to resist excessive rotation of the bond systems at nitrogen atoms; such rotation, though prerequisite to the existence of E, increases the difficulty of ring closure for G. The various data educed in discussing ring closure for G, buttressed by the bond angle sum and the possibly significant difference in averaged Co–O_G and Co–O_R bond lengths (definitely significant for the one Co–O_R distance), suggest considerable additional strain in G as compared with R rings, and, perforce, a definitely lower stability of the former.

Of the two stereoisomers of a quinquedentate octahedral complex derivable by opening, respectively, an R or a G ring, we expect the latter to be the more stable. Otherwise put, the more stable stereoisomer will have the void (or monodentate ligand) trans to one of the nitrogen atoms. In the following paper, which reports the structure of Ni(OH$_2$)H$_2$Y, the utility of this principle is clearly illustrated.

The anions are oriented in the crystal with an octahedral face defined by O_5, O_7, O_8 of each nearly parallel to (100). As the unit cell is but one anion thick along a, the $O_5O_7O_8$ plane approaches the nearly parallel plane defined by methylene carbons C_1, C_2, C_3 of the next anion along a. Assuming reasonable hydrogen positions, we find that the packing along a is consistent with normal van der Waals interactions corresponding to carbon–oxygen distances of 3.27, 3.52, 3.42 Å., respectively, for $C_2\cdot \cdot O_8$, $C_1\cdot \cdot O_5$, $C_5\cdot \cdot O_7$.

The packing relations perpendicular to a are shown in Fig. 5 for NH$_4$CoY·2H$_2$O. Co, NH$_4^+$, H$_2$O$_I$, H$_2$O$_{II}$ positions are all approximately in the planes $x = ^1/_4$, $^3/_4$, as indicated on the diagram. Dotted lines indicate possible hydrogen bonds. Distances from an ammonium ion to its near neighbors are: (A) 2.78 Å. to carbonyl O_2; (B) 2.71 Å. to H$_2$O$_I$; (C) 3.01 Å. to carbonyl O_1; (D) 2.98 Å. to carbonyl O_4; (E) 3.10 and 3.45 Å. to
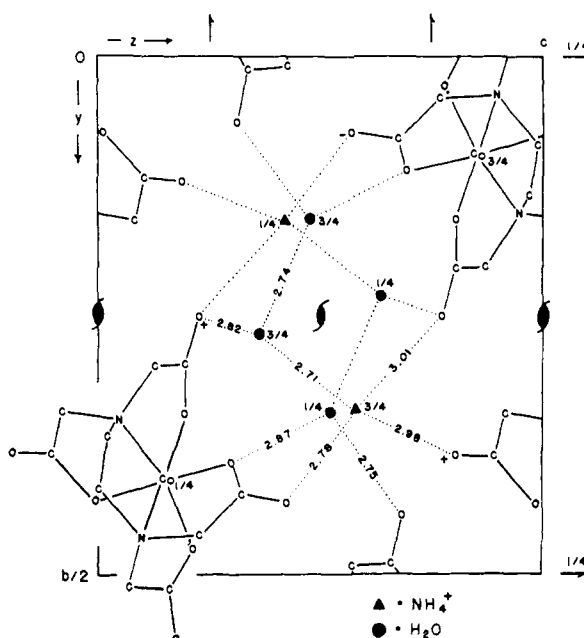

Fig. 5.—Packing relations perpendicular to short axis. Dotted lines indicate possible hydrogen bonds. A sign (+ or –) at carbonyl oxygen indicates connection to oxygen of an adjacent complex (above or below).

H$_2$O$_{II}$ above and below; (F) 3.31 Å. to carbonyl O_3. A and B presumably represent hydrogen bonds with bond angle at nitrogen at 91°. The configuration of the set A–D is, as is seen from Fig. 5, too nearly planar for C and D also to represent well directed hydrogen bonds. Angles at nitrogen between various bond pairs are: AC, 161°; BD, 146°; CD, 84°; BC, 96°; AD, 107.6°. Moreover, the lengths of C and D are definitely long for well directed bonds.

H$_2$O$_I$ is hydrogen bonded to NH$_4^+$ through B, and is (G) 2.74 Å. from H$_2$O$_{II}$, (H) 2.82 Å. from carbonyl O_1. Angles at O_I between bond pairs are: BG, 115.7°; GH, 95.9°; BH, 103.8°. H$_2$O$_{II}$ is hydrogen bonded to H$_2$O$_I$ through G, and is (J) 2.75 Å. from carbonyl O_3, (K) 2.87 Å. from ring O_6. Angles at O_{II} between bond pairs are: GJ, 118.6°; GK, 132.5°; JK, 86.3°. The fitting with the surely established G is better for J than for K, in agreement with the bond distances.

The packing pattern in RbCoY·2H$_2$O is even looser along b and c. Distances from a rubidium ion to its near neighbors are: 2.82 Å. to carbonyl O_2 and to H$_2$O$_I$; 2.89 Å. to carbonyl O_4; 2.93 Å. to carbonyl O_1; 3.09 Å. to carbonyl O_3; 3.25 and 3.34 Å. to H$_2$O$_{II}$, above and below. The four hydrogen bonds G, H, J, K become 2.77, 2.93, 2.80, 2.91 Å., respectively.

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