The Crystal Structures of Rubidium Hydrogen Croconate and Ammonium Hydrogen Croconate

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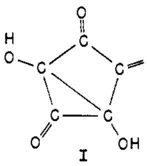
Abstract: The crystal structures of $RbHC_5O_5$ and $NH_4HC_5O_5$ were determined by single crystal methods. The monobasic anions form long planar chains through the cell due to hydrogen bond formation. The hydrogen bond formation destroys the expected mirror symmetry of the anion, and as a result the double bond appears not to be delocalized completely. The O-H···O distances are 2.50 and 2.46 Å.

Croconic acid is a dibasic acid first prepared by Gmelin.[1] As a result of early studies on this compound, some differences in opinion as to the positions of the hydroxyl groups arose. From the small difference in pK_1 and pK_2 values, Carpeni[2] concluded that the earlier idea of nonadjacent hydroxyl groups[3] was correct (I). Hirato, *et al.*,[4] first pictured croconic acid as a mixture of structures I, II, and III. Later, Hirato, Mizuno, and Yamada[5] showed that their ultraviolet spectroscopic measurements could be explained if form II exists in acid solution and form IV in basic solutions (dianion stabilized by resonance).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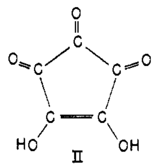
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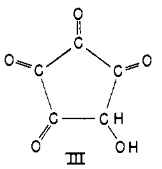
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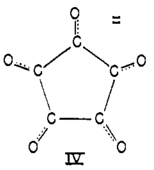
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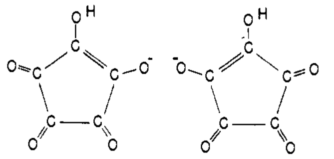
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West, *et al.*,[6-8] prepared salts of the croconate ion and a number of other related species. From infrared and Raman data they found that the croconate anion should possess D_5h symmetry. They also carried out simple molecular orbital calculations on a whole series of oxygenated anions.[9] The crystal structures of diammonium croconate[10] and copper croconate[11] showed conclusively that the dianion exists with D_5h symmetry.[10] The structure of the Zn salt of the croconate ion,[11] however, showed a distorted anion of an ene-diol form, due to the partially covalent bonds formed to zinc.

Solutions of croconic acid in water contain three species, the acid, the monoanion, and the dianion. Two equivalent valence bond structures can be written for the monoanion (V). The crystal structure determinations of the rubidium and ammonium salts of this monoanion are described below.

Experimental Section

Rubidium Hydrogen Croconate. A rubidium salt of croconic acid was made from a pure aqueous solution of the acid prepared by the method of Nietzki and Benckiser[3] by adding a 10% excess of RbCl for complete substitution of rubidium chloride and slowly cooling the hot saturated solution. Carbon-hydrogen analysis (*Anal.* Calcd: C, 26.42; H, 0.60. Found: C, 26.49; H, 0.44), differential thermal analysis, and density determination from X-ray data confirm that the salt is $RbHC_5O_5$.

Single crystal X-ray diffraction patterns were obtained for the zero through six upper layers about the *b* axis using a Weissenberg camera with Cu $K\alpha$ radiation (920 independent reflections). The multiple film technique was employed using three films, and a relative intensity scale was prepared from the single crystal under investigation. Since the product of the linear dimensions of the crystal employed (0.11×0.27 mm) times its linear absorption coefficient ($\mu = 115\ cm^{-1}$) is approximately equal to the crystal employed by Evans[12] (0.16×0.07, $\mu = 205\ cm^{-1}$) to make absorption contours on a Weissenberg plot, this absorption correction, as well as the Lorentz polarization correction, was applied to all the data.

The crystals of rubidium hydrogen croconate belong to the monoclinic system with $a = 7.861 \pm 0.005$, $b = 10.512 \pm 0.005$, $c = 7.819 \pm 0.005$ Å, $\beta = 102.5°$. With four molecules per unit cell, the calculated density is 2.385 compared to the pycnometric value of 2.436 g/cm³. The general conditions for reflections lead to the unique space group, $P2_1/c$. It was also noted that, in addition to the conditions that $(h0l)$ is present only if $l = 2n$, for the (hkl) data reflections were strong only when $l = 2n$ and $h = 4n$, and $l = 2n + 1$ for $h = 2n + 2$.

Owing to the additional conditions for strong reflections which exist, almost all scattering matter must lie in the *x*, *z* planes at $y = {}^1/_8$, ${}^3/_8$, ${}^7/_8$, or ${}^5/_8$, or it must mirror these planes. The four rubidium ions in the unit cell must occupy positions in the general set and must have a *y* parameter of ${}^1/_8$ in order to explain the regularities in the intensities. A Patterson projection on (010) plus a Harker section at $y = {}^1/_4$ located the rubidium ion at 0.198, 0.125, 0.052, which turned out to be very near the final position. Electron density methods enabled the rest of the structure to be determined, especially after attempts to place all scattering matter in planes at odd multiples of $y = {}^1/_8$ were discarded.

Since the structural work on this compound was begun about 10 years ago, the early refinement steps used techniques and computing facilities of that time (desk calculators, IBM 407 tabulators, and finally a diagonal least-squares program on the IBM 704). The last least-squares program using individual isotropic temperature factors gave an *R* value of 0.15. Some of the C–C and C–O distances appeared unreasonable, however. As a consequence, work was begun on the possibly isostructural ammonium ion analog.

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Table I. Atomic Parameters for Rubidium and Ammonium Hydrogen Croconate

	Rubidium hydrogen croconate		Ammonium hydrogen croconate	
		s^a		s
O_1 x	0.9678	0.002	0.9651	0.0008
y	0.1144	0.003	0.1194	0.0024
z	0.7081	0.002	0.7128	0.0008
$b_{11}{}^b$	0.0192	0.003	0.0080	0.0015
b_{22}	0.0183	0.004	0.0141	0.0015
b_{33}	0.0130	0.003	0.0034	0.0015
b_{12}	0.0146	0.007	0.0078	0.006
b_{13}	−0.0170	0.005	−0.0223	0.002
b_{23}	−0.0114	0.007	−0.0035	0.006
O_2	0.7773	0.002	0.7739	0.0015
	0.8799	0.004	0.8958	0.0011
	0.5470	0.002	0.5428	0.0015
	0.0264	0.004	0.0328	0.003
	0.0048	0.005	−0.0027	0.001
	0.0177	0.003	0.0082	0.002
	0.0251	0.008	0.0095	0.004
	0.0015	0.005	−0.0003	0.003
	−0.0062	0.008	−0.0011	0.003
O_3	0.5168	0.002	0.5134	0.0014
	0.9873	0.003	0.9860	0.0015
	0.2313	0.002	0.2338	0.0016
	0.0262	0.005	0.0144	0.003
	0.0049	0.004	0.0015	0.002
	0.0126	0.005	0.0081	0.003
	0.0038	0.005	−0.0048	0.003
	−0.0190	0.008	0.0041	0.004
	−0.0081	0.004	0.0080	0.003
O_4	0.5100	0.002	0.5040	0.0015
	0.2518	0.004	0.2524	0.0015
	0.2406	0.002	0.2443	0.0015
	0.0027	0.003	0.0090	0.002
	0.0155	0.005	0.0027	0.002
	0.0157	0.005	0.0186	0.004
	0.0062	0.004	−0.0022	0.003
	0.0033	0.004	−0.0292	0.004
	−0.0036	0.005	−0.0022	0.003
O_5	0.8120	0.002	0.8037	0.0014
	0.3412	0.003	0.3467	0.0013
	0.5257	0.002	0.5268	0.0016
	0.0130	0.003	0.0103	0.002
	0.0090	0.005	0.0068	0.002
	0.0130	0.002	0.0115	0.002
	−0.0052	0.005	−0.0096	0.004
	−0.0089	0.006	0.0013	0.003
	0.0024	0.005	−0.0137	0.004
C_1	0.8497	0.002	0.8418	0.0011
	0.1174	0.003	0.1104	0.0027
	0.5793	0.002	0.5921	0.0013
	0.0118	0.003	0.0028	0.002
	−0.0056	0.003	0.0088	0.002
	0.0189	0.004	0.0049	0.002
	0.0010	0.007	0.0100	0.005
	0.0030	0.005	0.0068	0.004
	−0.0096	0.007	0.0094	0.005
C_2	0.7479	0.002	0.7535	0.0024
	0.9952	0.004	0.0024	0.0018
	0.5122	0.003	0.4967	0.0027
	0.0047	0.003	0.0102	0.004
	0.0016	0.008	0.0130	0.003
	0.0113	0.004	0.0046	0.004
	−0.0048	0.006	−0.0106	0.007
	0.0141	0.005	0.0199	0.006
	−0.0189	0.006	−0.0015	0.007
C_3	0.6216	0.003	0.6169	0.0021
	0.0437	0.004	0.0553	0.0019
	0.3468	0.003	0.3650	0.0025
	0.0190	0.005	0.0140	0.003
	−0.0050	0.005	0.0050	0.005
	0.0119	0.004	0.0034	0.008
	0.0094	0.007	−0.0199	0.006
	0.0032	0.004	−0.0080	0.005
	−0.0024	0.007	0.0003	0.005
C_4	0.6200	0.002	0.6124	0.0017
	0.1768	0.004	0.1880	0.0019
	0.3524	0.002	0.3416	0.0027
	0.0040	0.004	−0.0054	0.002
	0.0100	0.006	0.0054	0.002
	0.0063	0.004	0.0169	0.004
	−0.0011	0.005	−0.0015	0.004
	0.0031	0.005	0.0065	0.005
	0.0033	0.006	−0.0028	0.005
C_5	0.7565	0.004	0.7637	0.0021
	0.2282	0.005	0.2333	0.0019
	0.4903	0.003	0.4944	0.0024
	0.0151	0.005	0.0004	0.003
	0.0397	0.012	0.0093	0.003
	0.0063	0.004	0.0033	0.003
	−0.0490	0.011	0.0026	0.005
	−0.0130	0.007	0.0045	0.005
	0.0240	0.008	−0.0163	0.005
Rb	0.1973	0.0003	0.1907	0.0008
	0.1253	0.0005	0.1239	0.0016
	0.0520	0.0003	0.0659	0.0008
	0.0130	0.0003	0.0069	0.002
	0.0070	0.0004	0.0078	0.001
	0.0124	0.0004	0.0049	0.002
	0.0000	0.0011	0.0060	0.005
	−0.0075	0.0004	0.0097	0.007
	−0.0004	0.0011	0.0078	0.004

[a] s is the estimate of the standard deviation. [b] Anisotropic temperature factor = $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$.

The refinement of the rubidium structure has been recently continued using full-matrix least-squares methods (IBM 7044) and anisotropic temperature factors on all atoms. The starting parameters were the final values of the ammonium hydrogen croconate refinement below. The discrepancy factor $R_w = \Sigma w|\Delta F|/\Sigma w|F_o|$ decreased to 0.104. The function $\Sigma w(F_o{}^2 - F_c{}^2)^2$ was minimized. Weights were chosen as $(F^2/C)^2$ for F^2 less than C, and $(C/F^2)^2$ for F^2 greater than C, where C was approximately $F^2{}_{max}/16$. Calculated and observed F values are available.[13]

Ammonium Hydrogen Croconate. Crystals were prepared from an equimolar mixture of diammonium croconate and croconic acid in water. Multiple film single crystal patterns were made by the Weissenberg method (Cu Kα) rotating about the b axis, $h0l$ to $h7l$. Precession films were made with Mo Kα radiation, $0kl$ to $3kl$; $hk0$ to $hk3$ (1024 independent reflections). The unit cell dimensions determined from back-reflection Weissenberg photographs (a, c, β) and from precession films (b) gave a = 7.708 ± 0.001, b = 10.496 ± 0.008, c = 7.820 ± 0.002 Å, β = 102.26 ± 0.02°, space group $P2_1/c$. Intensities were estimated visually; Lorentz polarization corrections were made, but absorption corrections were not.

Least-squares refinement was begun using parameters from the rubidium salt after the isotropic refinement. When agreement no longer improved with individual isotropic temperature factors, equivalent reflections in the different sets of data were averaged, and the refinement was continued with anisotropic temperature factors and a single scale constant. Hydrogen atoms were also included in the calculation (but not refined) in the last least-squares cycles. The hydrogen atoms did not appear clearly defined on difference electron density maps and so were placed in roughly appropriate positions to allow some hydrogen bonding. The final R_w was 0.079. Calculated and observed F values are available.[13]

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(13) A list of calculated and observed structure factors has been deposited as Document No. 8603 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. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table II. Interatomic Distances in Rubidium and Ammonium Hydrogen Croconate (in Å)

	Rb	*s*		NH_4	Av	Av	ZnC_5O_5	CuC_5O_5	$(NH_4)_2$-C_5O_5
C_1–O_1	1.21	0.02	C_1–O_1	1.19	0.01	1.20	1.274	1.249	1.269
C_5–O_5	1.27	0.06	C_2–O_2	1.18	0.02	1.22	1.186	1.240	1.241
C_4–O_4	1.34	0.04	C_3–O_3	1.37	0.02	1.36	1.247	1.276	1.289
C_3–O_3	1.23	0.03	C_4–O_4	1.21	0.02	1.22	1.254	1.243	1.241
C_2–O_2	1.25	0.05	C_5–O_5	1.24	0.02	1.24	1.217	1.240	1.269
C_1–C_5	1.47	0.06	C_1–C_2	1.44	0.03	1.45	1.484	1.457	1.463
C_5–C_4	1.45	0.04	C_2–C_3	1.42	0.02	1.43	1.480	1.446	1.452
C_4–C_3	1.40	0.06	C_3–C_4	1.40	0.03	1.40	1.415	1.432	1.452
C_3–C_2	1.54	0.02	C_4–C_5	1.56	0.02	1.55	1.475	1.491	1.463
C_2–C_1	1.54	0.05	C_5–C_1	1.55	0.03	1.55	1.501	1.459	1.455
Rb–O_1	2.90	0.01	NH_4–O_1	2.94	0.01				
Rb–O_2	3.10	0.01	NH_4–O_2	3.02	0.01				
Rb–O_2	2.81	0.04	NH_4–O_2	3.01	0.02				
Rb–O_3	2.98	0.02	NH_4–O_3	2.94	0.02				
Rb–O_4	2.90	0.02	NH_4–O_4	2.86	0.02				
Rb–O_5	3.04	0.03	NH_4–O_5	3.00	0.02				
Rb–O_5	3.01	0.02	NH_4–O_5	2.95	0.02				
O_4–H···O_3	2.50	0.05	O_3–H···O_4	2.46	0.02				

Discussion of the Structures

Although it was assumed in refining these structures that they were isostructural, the final positions of the atoms indicate that they are not arranged in exactly the same fashion. The list of parameters and their standard deviations are given in Table I. Though many of the atom parameters are identical in the two structures (using three standard deviations as a criterion), a number are clearly different. These are different in such a manner that the orientation of the anion differs in the two salts by an approximate mirroring along *b* (compare Figures 1 and 2).

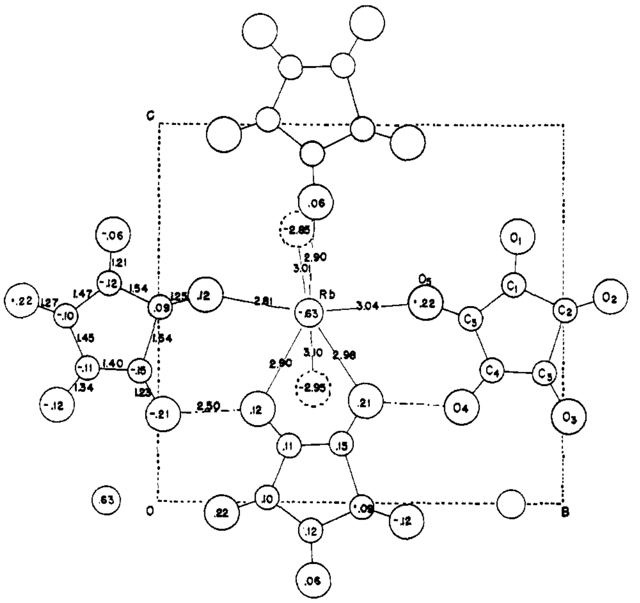

Figure 1. Projection of the rubidium hydrogen croconate structure on to the (101) plane ((100) plane of the $P2_1/n$ cell). Numbers inside the circles give the elevation in Å from the plane at $x = {}^3/_4$.

The ions lie in a plane parallel to the (101) plane. If one chooses new monoclinic cell dimensions, $A = -a$, $B = -b$, $C = a + c$, symmetry becomes $P2_1/n$ and

		Rb	NH_4
A	=	7.861	7.708
B	=	10.512	10.496
C	=	9.814	9.744
β	=	128.90	128.40

The ions now lie in planes parallel to (100) at about $^1/_4$ and $^3/_4$ along *a*. Figures 1 and 2 are normal projections onto the (100) plane, and deviations of the atoms from the plane at $x = {}^3/_4$ are given in Å. In both structures the ions are very nearly planar. The ions are tied together in linear strings by a short O–H···H bond of 2.46 (NH_4) and 2.50 Å (Rb). The coordination about the Rb^+ ion is sevenfold, having a pentagonal oxygen base on one side and two additional oxygen atoms on the other side of the metal ion. The two oxygen atoms belong to the anion layer one-half a unit cell away from the layer containing the pentagonal

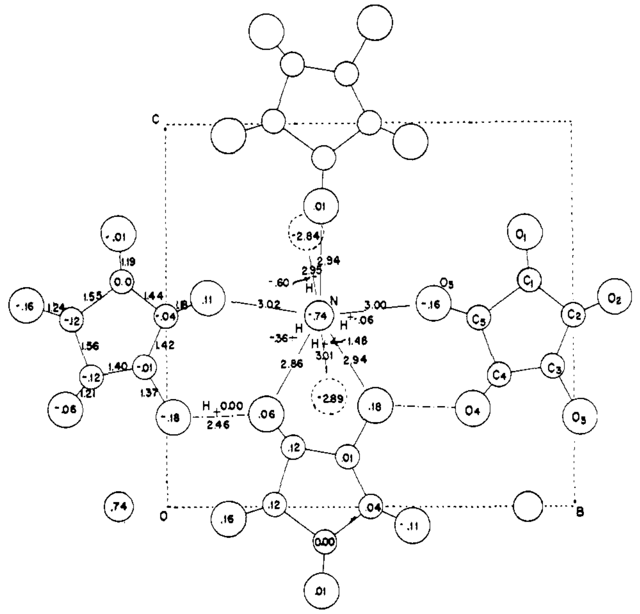

Figure 2. Projection of the ammonium hydrogen croconate structure onto the (101) plane ((100) plane of the $P2_1/n$ cell). Numbers inside the circles give the elevation in Å from the plane at $x = {}^3/_4$. Positions of H atoms are given by crosses with their elevation immediately adjacent.

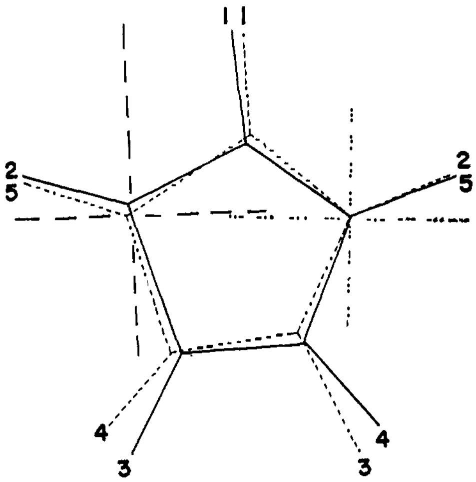

Figure 3. Comparison of the shape of the croconate ions from the two structures. The ion from the rubidium salt is shown in solid lines.

set of oxygen ligands. The dimensions of the unit cells differ mainly in the *A* direction, which determines the distance between the anion layers.

The interatomic distances and their standard deviations are given in Table II. The bond distances are fortuitously very similar, considering the magnitude of the standard deviations. An average value of these distances does not deviate significantly from the values reported earlier[14] from a preliminary stage of refinement. It is clear from the results, however, that the anion, rather than having the mirror symmetry as indicated by V, has had the double bond position partially stabilized by the hydrogen bond formation, such that in valence bond terms, one of the two valence bond structures is preferred more than the other. The dimensions are compared with those of the copper, zinc, and ammonium croconates in Table II.

Table III. Bond Angles in Rubidium and Ammonium Hydrogen Croconate

	Rubidium			Ammonium	
	L, deg	*s*, deg		L, deg	*s*, deg
O_1–C_1–C_5	128.9	4.5	O_1–C_1–C_2	132.8	2.8
O_1–C_1–C_2	120.5	3.5	O_1–C_1–C_5	118.9	2.4
C_2–C_1–C_5	109.2	2.4	C_5–C_1–C_2	107.8	1.2
C_1–C_5–O_5	121.6	2.6	C_1–C_2–O_2	124.8	1.4
O_5–C_5–C_4	132.2	4.4	O_2–C_2–C_3	128.7	3.2
C_4–C_5–C_1	105.7	4.7	C_3–C_2–C_1	105.3	2.1
C_5–C_4–O_4	122.2	5.4	C_2–C_3–O_3	124.1	2.4
O_4–C_4–C_3	125.1	3.0	O_3–C_3–C_4	115.8	1.5
C_3–C_4–C_5	112.7	2.9	C_4–C_3–C_2	118.4	2.4
C_4–C_3–O_3	119.6	2.5	C_3–C_4–O_4	129.1	2.4
O_3–C_3–C_2	131.6	4.9	O_4–C_4–C_5	128.1	3.1
C_2–C_3–C_4	108.3	2.9	C_5–C_4–C_3	102.1	1.3
C_3–C_2–O_2	124.0	3.6	C_4–C_5–O_5	124.2	1.7
O_2–C_2–C_1	132.3	1.2	O_5–C_5–C_1	129.9	1.6
C_3–C_2–C_1	101.7	3.1	C_4–C_5–C_1	105.8	1.7
C_4–O_4–O_3'	125.4	2.6	C_3–O_3–O_4'	120.7	1.6

The list of angles and their standard deviations are given in Table III. Though the bond lengths are similar in the two compounds, the angles are not nearly so identical. Figure 3 gives a graphic illustration of the similarity of the two ions. The ions have been superimposed so that the comparable bond distances coincide. The coordinate axes are also reproduced to show the extent of tilt as well as mirroring which the ions have undergone to place them in alignment. Although packing forces in the crystal might be expected to cause differences of the magnitude observed, they are more likely due to the uncertainties in their determination.

The anisotropic temperature factors undoubtedly served more to compensate for the systematic errors due to absorption than to represent atom vibrations. Hence, no attempt was made to analyze the parameters or to correct the bond distances for thermal motion.

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