James, R. W. & Brindley, G. W. (1931). *Z. Krystallogr.* **78**, 470.
Lipson, H. & Stokes, A. R. (1942). *Proc. Roy. Soc.* A, **181**, 101.
Lukesh, J. S. & Pauling, L. (1949). Paper presented at meeting of Crystallographic Society of America, April 1949 (abstract in *Amer. Min.* (1950), **35**, 125).
Lukesh, J. S. (1950). *Phys. Rev.* **80**, 226.
Magnus, A. (1923). *Ann. Phys., Lpz.* **70**, 303.
McWeeny, R. (1951). *Acta Cryst.* **4**, 513.
Nelson, J. B. & Riley, D. P. (1945). *Phil. Mag.* (7), **36**, 711.
Wilson, A. J. C. (1942). *Proc. Roy. Soc.* A, **180**, 277.
Wollan, E. O. & Shull, C. G. (1948). *Phys. Rev.* **73**, 830.

Acta Cryst. (1952). **5**, 499

The Crystal Structure of Ammonium Trioxalatochromate (III), $(NH_4)_3[Cr(C_2O_4)_3].2H_2O$

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The crystal structure of $(NH_4)_3[Cr(C_2O_4)_3].2H_2O$ is triclinic $P\bar{1}$, with two formula units in a cell of dimensions $a=7{\cdot}79$, $b=10{\cdot}90$, $c=10{\cdot}73$ Å, $\alpha=98°\ 10'$, $\beta=112°\ 36'$, $\gamma=67°\ 22'$. By evaluating the functions $\sigma(x, y)$, $\sigma(y, z)$ and $\sigma(x, z)$, projections of the structure on three crystallographic planes were obtained.

The 72 independant parameters of the 24 atoms comprising a formula unit are given, and the configuration of the two stereo isomeric complex ions $[Cr(C_2O_4)_3]$ in a unit cell is described. Each of the three oxalato groups in a complex ion is planar, the inner oxygen atoms of such groups forming a slightly distorted octahedron round the central chromium atom.

The ammonium ions and the water molecules form the main bonds in the structure. Two of the three ammonium ions approach each other to within a distance of 3·06 Å. This distance is considerably shorter than the other ammonium–ammonium distances, which are found to be 3·72 and 3·83 Å.

It is shown that this ammonium and the corresponding potassium structure are isotype if, for any one of these structures, the complex ions together with their associated cations are rotated through 180° about the central chromium atoms. It is further illustrated that such a rotation results in the novel feature that a $P(0, v, \frac{1}{2}c)$ Harker section then gives direct evidence as to whether similar unknown structures belong to the potassium or to the ammonium scheme of packing.

1. Introduction

The crystal structure of the corresponding potassium salt has been previously described by the authors (Niekerk & Schoening, 1952). It was pointed out in this publication that the presence of four comparatively heavy atoms in a formula unit, together with the fact that the crystal was treated throughout as belonging to the pseudo space group $C2/c$, severely restricted the accuracy with which interatomic distances for the complex ion $[Cr(C_2O_4)_3]$, could be determined by using the double Fourier series method. These difficulties do not appear in the corresponding ammonium salt. Furthermore, a preliminary investigation of these two salts (Niekerk & Schoening, 1951*b*) showed that they are not isomorphous as was previously reported by Wyrouboff (1900) and by Rammelsberg (1854). The potassium salt is monoclinic whereas the ammonium salt is triclinic, although its apparent monoclinic symmetry is very pronounced. The present investigation was therefore undertaken with the aim of obtaining more accurate interatomic distances for the complex ion, and if possible to determine why and how the two structures differ.

2. Crystal data and space group

The crystals were prepared by Mr du Plessis of the Pretoria University following the method described by Werner (1912*a*, *b*). The crystals are triclinic, dark blue in colour, and generally crystallize in the form of fairly thick plates. The primitive triclinic unit cell, as determined from oscillation and Weissenberg photographs, was found to be

$$a = 7{\cdot}79,\ b = 10{\cdot}90,\ c = 10{\cdot}73\ \text{Å}\,,$$
$$\alpha = 98°\ 10',\ \beta = 112°\ 36',\ \gamma = 67°\ 22'\,.$$

The space group can be either $P1$ or $P\bar{1}$. If, from chemical consideration and by analogy to the corresponding potassium salt, two stereo isomeric complex ions are assumed in the unit cell, the space group is then fixed as $P\bar{1}$. Density measurements and the successful structural analysis confirm the space group $P\bar{1}$.

The relation between the above triclinic unit cell and the monoclinic unit cell of the corresponding potassium salt has been previously described by the authors (Niekerk & Schoening, 1951*b*). In the potassium salt the faces {031} develop round the [100] zone, whereas in the ammonium salt the faces (010), $(010)_k$; (001), $(001)_k$; (011), $(021)_k$ and their opposite numbers develop round the [100] zone. The indices with suffix *k* are referred to a set of axes corresponding to those of the potassium salt.

In the literature (Wyrouboff, 1900; Rammelsberg, 1854) the compound is usually described as $(NH_4)_3[Cr(C_2O_4)_3].3H_2O$. It was found, however, that the crystals lose water in a dry atmosphere and absorb water in a humid atmosphere so that, although the crystals were coated with perspex films to prevent water loss during photographic exposures, the exact water content when an exposure was started remained uncertain. The following structural analysis indicates that for the crystal used in this analysis there are two water molecules associated with a formula unit.

3. Intensity measurements

The intensities of the reflections recorded from a small crystal on single and multiple Weissenberg films, using filtered Mo $K\alpha$ radiation, were estimated visually by comparing them with a standard set of spots of proportionately increasing exposure times. The observed intensities were corrected for the Lorentz and polarisation effects according to Kaan & Cole (1949). Absorption and extinction errors were neglected. By measuring a number of suitable spectra on a Geiger-counter X-ray spectrometer, using methods similar to those described by Cochran (1950) and Lonsdale (1948), it was possible to express all the intensities on an absolute scale.

4. Projections of the structure on three crystallographic planes

Taking as a starting point the co-ordinates found previously for the potassium salt, (substituting ammonium for potassium ions), the *b c* projection was evaluated first using the double Fourier series method. Successive refinements gave the final projection shown in Figs. 1 and 2. Structure factors were calculated using atomic scattering factors corrected for temperature effects. For carbon the values obtained by Robertson (1935) for anthracene were used. The oxygen and nitrogen values of James & Brindley (1931) were reduced proportionately. The excellent resolution of the atoms on this projection made it possible to deduce an empirical set of atomic scattering factors for chromium described previously by the authors (Niekerk & Schoening, 1951*c*). All the structure factors shown in Table 1 were calculated using these atomic scattering factor values.

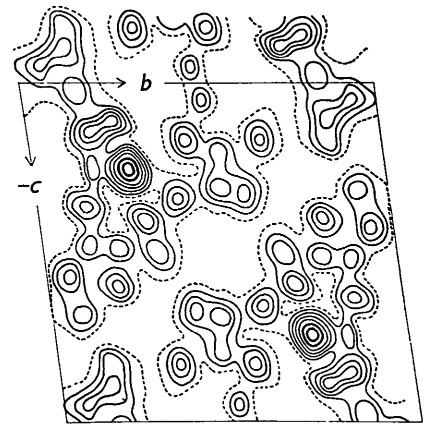

Fig. 1. Electron density projected against *a* on the *b c* plane. The contours are drawn at intervals of 2 e.Å^{-2}. The broken line is the two-electron contour. The heavy lines are the 20 and 30 e.Å^{-2} contours.

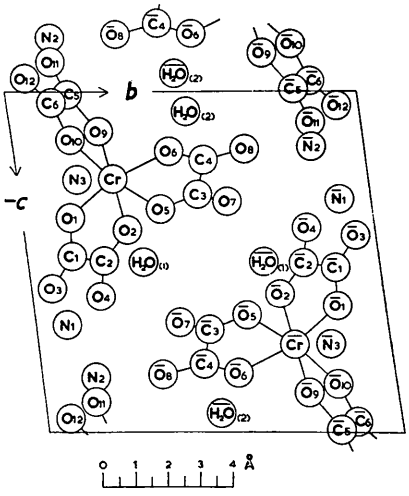

Fig. 2. Interpretation diagram for Fig. 1.

The projections finally obtained on the *a b* and *a c* planes are shown in Figs. 3, 4 and 5, 6, respectively. Owing to overlapping, the *x* co-ordinates obtained from the *a b* projection were uncertain in some cases. In order to obtain more accurate *x* co-ordinates for such atoms, the structure was also projected on the *a c* plane. For this projection only those structure factors which were used in evaluating the series $\sigma(x, z)$ were calculated. In all the projections the origin was taken as in *International Tables* for the space group $P\bar{1}$.

5. Estimation of parameters

The 72 independant parameters are shown in Table 2. The excellent agreement between the observed and calculated structure factors for the $0kl$ spectra (Table 1) shows that the *y* and *z* parameters are very reliable. Because of considerable overlapping in both

Fig. 3. Electron density projected against c on the $a\,b$ plane. The contours are as for Fig. 1 except that the heavy lines are the 18, 24 and 30 e.Å^{-2} contours.

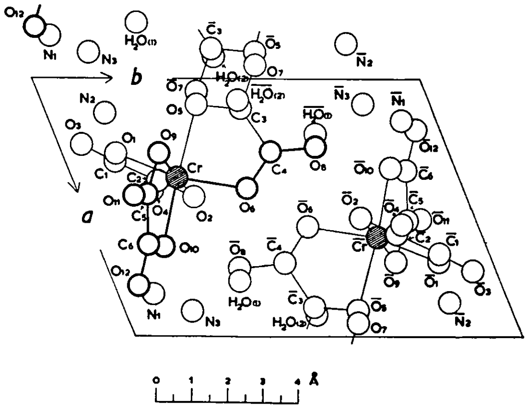

Fig. 4. Interpretation diagram for Fig. 3. Atoms joined by heavy lines lie above the chromium atom.

the $a\,b$ and $a\,c$ projections the x co-ordinates are less accurate.

6. Description of the complex ion $[Cr(C_2O_4)_3]$

Within the errors of experiment it is found that each of the three oxalato groups in a complex ion is planar. The six inner oxygen atoms of these groups surround the central chromium atom in an approximate octahedral configuration. The distances and angles in a complex ion are given in Table 3. These distances can be compared with those previously described by the authors (Niekerk & Schoening, 1951a) for the complex ion $[Cr(C_2O_4)_2(H_2O)_2]$, which are given in column 4 of this table, and also with those found by Robertson & Woodward (1936) for oxalic acid (column 5).

7. Discussion of the structure and the bonding

The two stereo isomeric ions in the unit cell are shown in Fig. 2. In this diagram the bar atoms are derived from the non-bar atoms by the operation of a symmetry centre. The oxalato arm $O_1O_2O_3O_4$ lies almost in the plane of the diagram. The arm marked $O_5O_6O_7O_8$ points slightly down in the negative a direction, whereas the arm $O_9O_{10}O_{11}O_{12}$ points up. The ammonium ions N_1, N_2 and N_3 lie approximately halfway between this complex ion and its repeat in the a direction. The complex ion comprised of bar atoms does not lie at the same level as the non-bar atoms complex ion, but approximately at $\frac{1}{2}a$ above the latter. The complex ions in the structure are therefore staggered in the a direction as can be seen from Fig. 4.

Fig. 5. Electron density projected along b on the $a\,c$ plane. The contours are drawn as for Fig. 3.

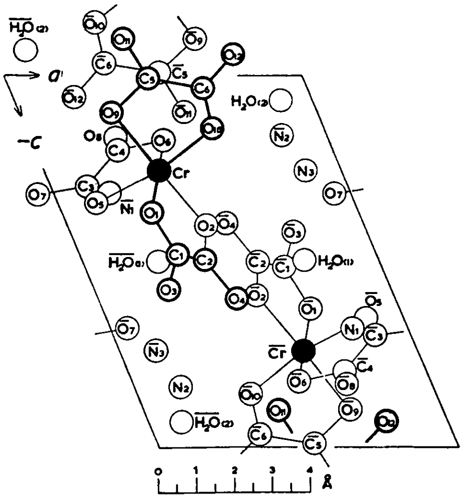

Fig. 6. Interpretation diagram for Fig. 5. Atoms joined by heavy lines lie above the chromium atom.

The ammonium ions and the water molecules seem to be mainly responsible for linking together the complex ions. The distances tabulated in Table 4 show the closest approach between atoms (see Fig. 2).

The ammonium ion marked N_2 has four nearest neighbours which are arranged in a deformed tetrahedron, together with four longer bonds. This tetrahedral surrounding strongly suggests the presence of hydrogen bridges $N–H \cdots O$. A similar arrangement has been found by Romers, Ketelaar & MacGillavry (1951) for the ammonium ions in ammoniumtetrametaphosphate. Such hydrogen bridges of length 2·8 Å

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
100	56	−73	037	12	−18	076	< 7	− 5
200	16	−15	038	7	+10	077	< 8	− 4
300	< 7	− 2	039	< 7	+ 6	078	< 8	+15
400	25	−25	$03\bar{1}$	100	−91	079	< 8	+ 6
500	< 8	− 5	$03\bar{2}$	8	−12	$07\bar{1}$	12	−13
600	< 8	−11	$03\bar{3}$	16	+12	$07\bar{2}$	13	−23
700	< 9	+ 1	$03\bar{4}$	< 5	+ 2	$07\bar{3}$	< 7	− 1
010	< 4	+ 6	$03\bar{5}$	38	−37	$07\bar{4}$	< 7	+11
020	44	−53	$03\bar{6}$	< 6	+ 8	$07\bar{5}$	< 7	− 9
030	47	−43	$03\bar{7}$	23	+20	$07\bar{6}$	7	−14
040	< 5	− 6	$03\bar{8}$	< 7	−11	$07\bar{7}$	< 8	+13
050	22	−30	$03\bar{9}$	< 7	− 2	$07\bar{8}$	11	+16
060	< 6	+ 2	041	14	+12	$07\bar{9}$	8	− 7
070	26	+21	042	< 5	+ 2	081	29	−21
080	< 7	+ 5	043	16	+10	082	< 7	− 1
090	23	−24	044	25	+27	083	22	+21
0,10,0	< 8	− 7	045	17	−14	084	< 7	+ 3
0,11,0	< 8	0	046	23	−25	085	21	−25
0,12,0	< 9	0	047	30	+30	086	< 8	− 8
001	7	− 2	048	< 7	+12	087	< 8	+ 5
002	26	−21	049	< 8	− 5	$08\bar{1}$	33	+35
003	< 4	− 2	$04\bar{1}$	< 5	+ 5	$08\bar{2}$	14	−15
004	< 5	+ 2	$04\bar{2}$	44	−40	$08\bar{3}$	7	−10
005	10	−14	$04\bar{3}$	19	−17	$08\bar{4}$	< 7	+ 2
006	< 6	−10	$04\bar{4}$	30	+32	$08\bar{5}$	< 7	− 5
007	< 6	0	$04\bar{5}$	12	+ 5	$08\bar{6}$	< 8	− 4
008	14	+14	$04\bar{6}$	36	−32	$08\bar{7}$	11	−17
009	20	−19	$04\bar{7}$	10	−17	$08\bar{8}$	8	+ 9
0,0,10	< 8	− 4	$04\bar{8}$	10	+ 5	$08\bar{9}$	9	+12
011	41	−46	$04\bar{9}$	< 8	− 5	091	< 7	− 8
012	62	+53	051	11	−28	092	21	+27
013	30	+29	052	19	−26	093	24	−14
014	9	−11	053	16	+24	094	11	−18
015	16	−22	054	15	−14	095	< 8	− 6
016	< 6	− 8	055	< 6	+ 8	096	12	+18
017	25	+38	056	30	+35	097	< 8	− 6
018	< 7	+ 6	057	10	+19	$09\bar{1}$	< 7	0
019	27	−26	058	< 7	− 4	$09\bar{2}$	7	+ 7
$01\bar{1}$	58	+56	059	< 7	+ 3	$09\bar{3}$	11	−16
$01\bar{2}$	51	+36	$05\bar{1}$	20	+18	$09\bar{4}$	< 8	− 6
$01\bar{3}$	30	−27	$05\bar{2}$	39	+35	$09\bar{5}$	< 8	+ 3
$01\bar{4}$	< 5	+ 3	$05\bar{3}$	19	−20	$09\bar{6}$	14	+16
$01\bar{5}$	34	+37	$05\bar{4}$	29	−30	$09\bar{7}$	12	−11
$01\bar{6}$	16	−17	$05\bar{5}$	< 6	+ 1	0,10,1	8	+ 6
$01\bar{7}$	23	−19	$05\bar{6}$	< 7	+ 7	0,10,2	< 8	+ 2
$01\bar{8}$	10	+14	$05\bar{7}$	20	−15	0,10,3	< 8	− 2
$01\bar{9}$	23	+28	$05\bar{8}$	< 7	− 1	0,10,4	< 8	+ 3
021	26	+38	$05\bar{9}$	< 7	+11	0,10,5	< 8	+ 4
022	< 4	+13	061	36	+36	0,10,6	< 9	− 6
023	50	+47	062	< 6	0	0,10,7	15	−14
024	15	−16	063	12	−18	$0,10,\bar{1}$	19	−23
025	19	+13	064	16	− 9	$0,10,\bar{2}$	< 8	− 3
026	24	+22	065	25	+32	$0,10,\bar{3}$	22	+26
027	20	−24	066	12	+19	$0,10,\bar{4}$	< 8	− 3
028	30	−39	067	< 7	−12	$0,10,\bar{5}$	12	−10
029	< 7	+ 1	068	< 8	+11	0,11,1	< 8	− 5
$02\bar{1}$	< 3	+ 4	069	< 8	0	0,11,2	15	−14
$02\bar{2}$	19	+28	$06\bar{1}$	20	−18	0,11,3	< 8	− 4
$02\bar{3}$	21	+11	$06\bar{2}$	42	+40	0,11,4	12	+10
$02\bar{4}$	15	−21	$06\bar{3}$	19	−17	$0,11,\bar{1}$	< 8	+ 3
$02\bar{5}$	< 5	− 3	$06\bar{4}$	< 7	− 4	$0,11,\bar{2}$	17	−20
$02\bar{6}$	26	+26	$06\bar{5}$	< 7	−11	$0,11,\bar{3}$	< 8	0
$02\bar{7}$	< 6	+ 1	$06\bar{6}$	7	+ 5	0,12,1	< 9	− 8
$02\bar{8}$	41	−43	$06\bar{7}$	12	+ 9	0,12,2	< 9	− 9
$02\bar{9}$	20	+16	$06\bar{8}$	15	−16	0,12,3	13	+10
031	42	+24	$06\bar{9}$	14	−18	0,12,4	< 9	+ 1
032	< 4	+ 5	071	22	+13	0,12,5	14	−13
033	16	−18	072	27	−28	$0,12,\bar{1}$	18	+15
034	36	+31	073	< 7	+ 1	110	49	−46
035	18	+27	074	7	+ 3	120	46	+80
036	30	−30	075	7	+ 9	130	48	+41

Table 1 (*cont.*)

hkl	F_o	F_c
140	< 5	−3
150	< 7	−9
160	13	+19
170	< 7	0
180	25	−23
190	< 8	−9
1,10,0	< 9	+12
1,11,0	24	−15
$\bar{1}10$	26	+9
$\bar{1}20$	56	+96
$\bar{1}30$	7	−19
$\bar{1}40$	40	−30
$\bar{1}50$	40	+36
$\bar{1}60$	14	−5
$\bar{1}70$	50	−53
$\bar{1}80$	25	+29
$\bar{1}90$	< 9	+6
210	40	+30
220	22	+3
230	62	−74
240	41	+34
250	75	+66
260	32	−29
270	19	+11
280	< 8	+8
290	< 8	+2
2,10,0	< 9	0
2,11,0	19	+7
$\bar{2}10$	77	−77
$\bar{2}20$	33	−35
$\bar{2}30$	19	+14
$\bar{2}40$	13	−8
$\bar{2}50$	18	−17
$\bar{2}60$	24	+26
$\bar{2}70$	< 8	+14
$\bar{2}80$	< 9	−6
$\bar{2}90$	< 9	−10
$\bar{2}$,10,0	25	+18
310	58	−64
320	18	+14
330	< 6	+26
340	6	−3
350	24	−24
360	7	+5
370	15	+25
380	8	+13
390	14	+5
3,10,0	< 8	−4
3,11,0	9	+1
3,12,0	14	−12
$\bar{3}10$	41	+48
$\bar{3}20$	59	−60
$\bar{3}30$	< 7	+2
$\bar{3}40$	< 7	+16
$\bar{3}50$	< 8	0
$\bar{3}60$	12	−17
$\bar{3}70$	9	+6
$\bar{3}80$	26	+18
410	26	+13
420	20	+8
430	< 7	+4
440	47	−33
450	< 7	+5
460	< 7	−4
470	< 8	−4
480	12	−24
490	14	+23
4,10,0	9	−5
4,11,0	<10	−5
4,12,0	<10	+3
$\bar{4}10$	< 7	−4
$\bar{4}20$	17	+24
$\bar{4}30$	10	+26
$\bar{4}40$	< 8	−3
$\bar{4}50$	< 8	+7
$\bar{4}60$	9	+13
$\bar{4}70$	27	−22
510	< 7	+7
520	23	−34
530	< 7	+1
540	33	+34
550	< 8	−6
560	16	−33
570	< 8	−1
580	9	−6
590	< 9	−1
5,10,0	< 9	−2
5,11,0	10	+11
$\bar{5}10$	8	+13
$\bar{5}20$	< 7	+4
$\bar{5}30$	27	+25
$\bar{5}40$	< 9	+2
$\bar{5}50$	9	−9
610	21	+16
620	23	+22
630	12	+15
640	26	−27
650	29	−11
660	< 8	+5
670	< 9	+10
680	< 9	+2
690	< 9	−1
6,10,0	14	+13
$\bar{6}10$	< 9	+11
$\bar{6}20$	22	−17
$\bar{6}30$	13	−21
$\bar{6}40$	<10	0
710	< 9	−4
720	< 9	0
730	< 9	−11
740	< 9	+14
750	26	+21
760	< 9	+4
770	< 9	−15
780	<10	+8
790	<10	+9
7,10,0	13	−13
101	35	+62
201	42	−35
401	6	−18
$\bar{1}01$	51	−70
$\bar{2}01$	36	+48
$\bar{3}01$	14	−3
$\bar{5}01$	11	+10
102	24	−10
202	34	−7
302	48	−32
402	45	+45
602	11	+7
$\bar{3}02$	17	+9
$\bar{4}02$	42	+33
$\bar{5}02$	26	−32
$\bar{8}02$	12	−10
203	46	+64
303	34	−35
603	8	−7
$\bar{1}03$	49	+51
$\bar{2}03$	14	−38
$\bar{3}03$	5	+2
$\bar{4}03$	27	−35
$\bar{6}03$	18	+29
$\bar{7}03$	23	−25
104	15	+16
204	22	+20
404	25	−25
$\bar{1}04$	13	−35
$\bar{2}04$	36	−41
$\bar{3}04$	17	+22
$\bar{4}04$	19	−19
$\bar{5}04$	49	+49
$\bar{6}04$	15	−16
105	11	−9
205	15	−13
505	12	−13
605	13	+17
$\bar{1}05$	25	−35
$\bar{2}05$	32	+33
$\bar{3}05$	44	−46
$\bar{4}05$	34	+36
$\bar{6}05$	23	−24
$\bar{7}05$	16	+14
106	18	+29
$\bar{1}06$	26	+15
$\bar{2}06$	23	−22
$\bar{5}06$	22	−26
$\bar{8}06$	12	−9
107	12	−12
207	23	+27
$\bar{2}07$	18	−14
$\bar{3}07$	16	+13
$\bar{5}07$	12	−8
$\bar{6}07$	21	+24
$\bar{7}07$	17	−14
$\bar{8}07$	13	+17
108	21	−32
308	17	+15
408	13	−17
$\bar{1}08$	14	−21
$\bar{2}08$	7	+12
109	20	+11
$\bar{2}09$	10	+21
$\bar{4}09$	13	+8
$\bar{5}09$	8	−6
2,0,10	9	+10
$\bar{3}$,0,10	8	−7
$\bar{4}$,0,10	30	+34
$\bar{5}$,0,10	8	−9
$\bar{3}$,0,11	8	+16
$\bar{1}$,0,12	9	−11
$\bar{2}$,0,12	9	+12
$\bar{3}$,0,12	9	−6

have been reported in several other cases. The distances associated with N_1 and N_3 do not, however, form such a definite scheme of arrangement.

The closest approach between N_1 and N_2 and between N_2 and N_3 is 3·72 and 3·83 Å respectively. These distances are comparable with those found in other structures containing ammonium ions. The distance between N_1 and N_3, which is only 3·06 Å,

Table 2. *Final parameters*

Atom	x/a	y/b	z/c
O_1	0·300	0·137	−0·370
O_2	0·467	0·295	−0·405
O_3	0·250	0·058	−0·578
O_4	0·467	0·195	−0·602
O_5	0·127	0·398	−0·343
O_6	0·442	0·443	−0·175
O_7	−0·060	0·610	−0·320
O_8	0·283	0·660	−0·168
O_9	0·307	0·250	−0·100
O_{10}	0·627	0·167	−0·143
O_{11}	0·450	0·140	0·097
O_{12}	0·800	0·060	0·057
$H_2O_{(1)}$	0·750	0·328	−0·500
$H_2O_{(2)}$	0·825	0·500	−0·057
$NH_{4(1)}$	0·817	0·090	−0·685
$NH_{4(2)}$	0·133	0·150	−0·838
$NH_{4(3)}$	0·883	0·170	−0·257
C_1	0·330	0·128	−0·483
C_2	0·413	0·218	−0·497
C_3	0·117	0·510	−0·300
C_4	0·273	0·540	−0·200
C_5	0·477	0·177	−0·007
C_6	0·653	0·128	−0·033
Cr	0·385	0·273	−0·256

Table 3. *Dimensions of complex ion*

(All distances are in Ångström units and all angles in degrees)

Atoms	d	d mean	d dioxalato	d R. & W.*
Cr–O_1	1·93	1·96	1·93	—
Cr–O_2	2·01			
Cr–O_5	1·89			
Cr–O_6	2·06			
Cr–O_9	2·06			
Cr–O_{10}	1·83			
O_1–O_2	2·66	2·65	2·56	—
O_5–O_6	2·60			
O_9–O_{10}	2·68			
O_1–C_1	1·30	1·28	1·31	—
O_2–C_2	1·26			
O_5–C_3	1·23			
O_6–C_4	1·29			
O_9–C_5	1·34			
O_{10}–C_6	1·23	—	—	1·24 and 1·30
C_1–O_3	1·29	—	—	
C_2–O_4	1·31	1·31	1·28	—
C_3–O_7	1·35			
C_4–O_8	1·33			
C_5–O_{11}	1·35			
C_6–O_{12}	1·23	—	—	—
C_1–C_2	1·41	1·40	1·39	1·44
C_3–C_4	1·40			
C_5–C_6	1·39			
O_3–O_4	2·75	2·74	2·55	—
O_7–O_8	2·76			
O_{11}–O_{12}	2·71			
O_1–Cr–O_2		85°	83°	—
O_1–C_1–O_3		120°	125°	126°

* Robertson & Woodward (1936).

Table 4. *Closest approach between atoms*

Atom	Distance (Å)
N_1–O_{11}	2·83
O_{12}	2·70
O_3+a	3·00
O_4	2·95
$\overline{O}_8$	3·03
$H_2O_{(1)}$	3·04
$\overline{O}_1-b$	3·14
$\overline{N}_3-b$	3·06
N_2–O_3	2·78
O_{11}	2·78
$O_{12}-a$	2·90
$\overline{O}_7-a$	2·90
O_4	3·00
$\overline{O}_{12}-b$	3·09
$\overline{O}_8-a$	3·12
$\overline{O}_{10}-b$	3·25
N_3–O_{10}	2·72
O_2	2·85
$H_2O_{(1)}$	2·94
$\overline{O}_{12}-b$	3·11
$\overline{N}_1-b$	3·06
O_9+a	3·46
$H_2O_{(1)}$–N_1	3·04
N_3	2·94
O_2	2·91
O_5+a	3·10
$H_2O_{(2)}$–O_8	3·65
O_6	3·03
O_7+a	3·73
$\overline{H_2O}_{(2)}$	2·53

appears to be unusually short. Both N_1 and N_3 are clearly resolved in the *b c* projection. N_3 is also resolved in the *a b* projection. N_1, although not resolved in either the *a b* or the *a c* projections, can, however, be fixed with a fair degree of accuracy on both these projections since its *y* and *z* co-ordinates are accurately known. There seems to be little doubt therefore that this rather short N_1–N_3 distance is real.

8. Comparison between the K_3 and $(NH_4)_3$ structures

In order to describe the difference between the two structures, reference will be made to the diagrams of the potassium salt previously described by the authors (Niekerk & Schoening, 1952). For simplicity the letters A and K when written behind diagrams referred to in this section will mean that such diagrams refer to the ammonium or to the potassium structures respectively. The axis systems chosen for the two structures are such that the *a* and *c* axes are in structurally equivalent directions. The *b* axes differ in so far that, when the *b* axis of the potassium structure is referred to the ammonium structure, it lies in the plane of Fig. 4 A in a direction perpendicular to the *a* axis of this diagram.

Considering Figs. 3 K and 2 A, it would appear that the arrangement of complex ions in the two structures is practically identical. If, however, the $O_5O_6\bar{O}_5\bar{O}_6$ arms of units 1 and 2 (Fig. 3 K) are chosen as reference arms, then, because there is a glide plane at $(0, \frac{1}{4}, 0)$ with glide $\frac{1}{2}c$, it follows that corresponding atoms of such arms have the same x co-ordinate. This is clearly illustrated in Fig. 5 K, where one of these arms is marked with single and the other one with double circles. That this is not the case for the ammonium structure is clearly seen by inspecting the corresponding arms $O_5O_6O_7O_8$ and $\bar{O}_5\bar{O}_6\bar{O}_7\bar{O}_8$ in Fig. 4 A. By extending these observations to complete complex ion units in the two structures it becomes clear that, whereas units marked 1 and 2 in Fig. 3 K lie at the same height in the a direction, corresponding units in Fig. 2 A (indicated by non-bar and bar atoms respectively) are staggered at intervals of approximately $\frac{1}{2}a$ in the a direction.

In the following description it is shown how the potassium structure must be modified in order to obtain similar relative atomic positions for the potassium and the ammonium structures. This is best described by referring to Figs. 3 K and 2 A of the two structures. In Fig. 3 K, unit 2 is derived from unit 1 by the glide plane $(0, \frac{1}{4}, 0)$. Unit 3 is derived from unit 2 by the screw axis $(\frac{1}{2}, 0, \frac{3}{4})$, unit 3 lying at a distance of $\frac{1}{2}a$ above or below units 1 and 2, which lie at the same a level. Unit 3 and the repeat of unit 1 along c are therefore staggered in the a direction by an amount $\frac{1}{2}a$. As was pointed out above, a similar staggering applies to the non-bar and the bar units of the ammonium structure (Fig. 2 A), so that, for the units under consideration, their arrangement in the two structures is similar as regards the a direction. In order to obtain identical arrangements for the units under consideration it is only necessary now to perform in the $b\,c$ plane of the potassium structure (Fig. 3 K) a 180° rotation for every complex ion and its associated cations about the central chromium atom. Such a rotation reveals the important difference between the two structures. Whereas in the potassium structure (Fig. 3 K) the arms $O_5O_6\bar{O}_5\bar{O}_6$ point towards the glide plane $(0, \frac{1}{4}, 0)$ and the cations lie further away from this glide plane than the chromium atom, corresponding arms (marked $O_5O_6O_7O_8$) in the ammonium structure point away from the corresponding hypothetical glide plane, and the cations lie between the chromium atom and this glide plane.

The rotation of complex ions together with cations, as discussed above, has an interesting feature. If the cations in similar monoclinic (or nearly monoclinic) structures happen to be heavy atoms, their distances from the glide plane can be detected by evaluating the Harker section $P(0, v, \frac{1}{2}c)$. Such an evaluation will give direct evidence as to whether an unknown structure belongs to the potassium or to the ammonium scheme of packing.

It is difficult at this stage to decide what causes the difference between the ammonium and potassium structures. The ability of an ammonium ion to form tetrahedral hydrogen bonds may cause the difference. On the other hand, the difference in size between the ionic radii of potassium and ammonium ions may influence the arrangement of complex ions in the structure. This latter possibility is at present being investigated by the method outlined above for the corresponding rubidium and cesium salts, as for these salts the relevant ions, when arranged in order of increasing effective atomic radii according to Goldschmidt, follow the order K, Rb, NH_4, Cs.

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References

Cochran, W. (1950). *Acta Cryst.* **3**, 268.

James, R. W. & Brindley, G. W. (1931). *Phil. Mag.* **12**, 81.

Kaan, G. & Cole, W. F. (1949). *Acta Cryst.* **2**, 38.

Lonsdale, K. (1948). *Acta Cryst.* **1**, 12.

Niekerk, J. N. van & Schoening, F. R. L. (1951*a*). *Acta Cryst.* **4**, 35.

Niekerk, J. N. van & Schoening, F. R. L. (1951*b*). *Acta Cryst.* **4**, 381.

Niekerk, J. N. van & Schoening, F. R. L. (1951*c*). *Acta Cryst.* **4**, 382.

Niekerk, J. N. van & Schoening, F. R. L. (1952). *Acta Cryst.* **5**, 196.

Rammelsberg, K. F. (1854). *Ann. Phys., Lpz.* **93**, 50.

Robertson, J. M. (1935). *Proc. Roy. Soc.* A, **150**, 106.

Robertson, J. M. & Woodward, I. (1936). *J. Chem. Soc.* p. 1817.

Romers, C., Ketelaar, J. A. A. & MacGillavry, C. H. (1951). *Acta Cryst.* **4**, 114.

Werner, A. (1912*a*). *Ber. dtsch. chem. Ges.* **45**, 121.

Werner, A. (1912*b*). *Ber. dtsch. chem. Ges.* **45**, 3061.

Wyrouboff, M. G. (1900). *Bull. Soc. franç. Minér.* **5**, 65.