

ester formation or by repression of ionization increases the velocity constant over a hundred fold when the bromine is in the α -position to the group bearing the charge, but has little effect when the bromine is in the β -position. All of these facts are in accord with the predictions of the electrostatic theory of reaction velocity.

4. For the α -bromopropionate-thiosulfate reaction, the limiting slope predicted by the Brönsted-Debye theory is approached for concentrations less than $\sqrt{\mu} = 0.06$. For the β -bromopropionate-thiosulfate reaction the velocity constant contrary to this theory *increases* with decreasing $\sqrt{\mu}$ values, the effect being most marked in the very dilute region.

5. As an explanation of this anomalous result for the β -bromopropionate, a theory based on the assumption of oriented collision is submitted.

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THE CRYSTALLINE FORM OF SOME NEW COBALTAMMINES¹

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Introduction

The recent work of V. M. Goldschmidt on crystal chemistry has shown that crystal structure is determined by the relative numbers, size and deformability of the constituent particles.³ These results are based largely on x-ray investigation, but deal primarily with relatively simple compounds. The structure of a compound consists of an interpenetration of a definite anion and cation arrangement, whose mutual influence on each other determines the final structure of the compound. A given cation structure is expanded by the introduction of various anions, but this expansion has a limit, at which the fundamental cation arrangement alters. The substitution of various cations similarly influences the structure of the anion.

The cation of a complex cobaltamine must represent the largest and most determining part of the final structure of compounds containing this cation in combination with a simple anion. The structure of compounds of

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³ V. M. Goldschmidt, *Skrifter Norske Videnskap. Akad. Oslo*, 1926, No. 2; *ibid.*, 1926, No. 8; *Naturwissenschaften*, 14, 477 (1926); *Trans. Faraday Soc.*, 25, 253-83 (1929).

this type is determined to a large extent by the cation, whose fundamental arrangement can be altered only with great difficulty. The axial ratio of suitable cobaltamines containing various simple anions should offer a means of determining the effect which an anion produces on a given cation structure. It must be remembered that when the structure of the cation does not represent a large portion of the final structure, and when the cation is not complex and heterogeneous, the axial ratio will be inadequate to measure the effect which the anion produces, as is seen from Fig. 1.

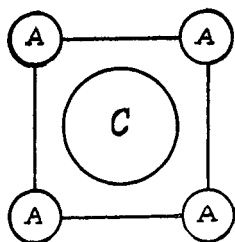


Fig. 1.—If the substitution of (C) increases the absolute dimension of the cell from 5×5 to 10×10 , the axial ratio is not changed.

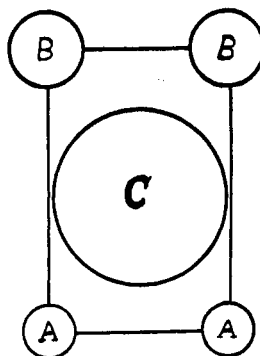


Fig. 1a.—If the substitution of (C) increases the absolute dimension of the cell from 4×10 to 8×12 , the axial ratio changes from 1:2.5 to 1:1.5.

Fig. 1.—Illustrating the type of atomic arrangement, whose expansion may be detected by axial ratio determinations.

The figures show that the effect of the anion can be measured by a determination of the axial ratios only in the second case, where various anions (C) expand the cation structure (AABB) to different extents in different directions depending upon the atoms involved in the expansion. Only x-ray measurements will ascertain the absolute expansion in either of the above cases, but any irregular expansion in different directions may be detected in the axial ratios as determined by geometrical crystallography. The acido cobaltamines are compounds of the type shown in Fig. 1a, and should be well suited for testing this view. The introduction of various anions will not produce any regular differences on the crystalline form of the compound if the new anion causes a change in structural type to occur. However, the structural type of the compounds reported in this paper appears to be the same, and regular differences in the crystalline form should be and are observed.

Experimental

Preliminary work showed that compounds in the oxalato series were very stable and could be obtained in measurable crystals; therefore, several oxalato tetrammines were prepared, analyzed and their crystalline form determined. None of the compounds studied, except the perchlorate, has been previously described; therefore their methods of preparation and properties are included in this paper.

Preparation of Compounds.—Oxalato tetrammine cobalti sulfate was first prepared by the method of Schramm, and this was used to prepare the other compounds in the oxalato series.⁴

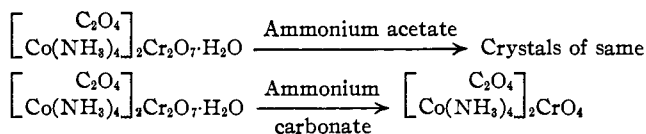
1. **Oxalato Tetrammine Cobalti Dichromate.**—A saturated solution of potassium dichromate at 30 to 40° is added slowly and with stirring to a saturated solution of the oxalato sulfate. A few drops of acetic acid or a little ammonium acetate is added to the oxalato sulfate solution to prevent decomposition. A bright orange-red precipitate is formed, which is filtered off at once, washed with cold water and alcohol, then dried in the air. The precipitate is a mass of minute but perfect crystals.

Constituent	Composition $[\text{Co}(\text{NH}_3)_4]_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$	
	Calcd., %	Found, %
Cr	15.66	15.69
Co	17.76	18.21
NH ₃	20.513	20.55
H ₂ O	2.712	2.71
C ₂ O ₄	Not determined	

The salt was found to be more soluble in a solution of ammonium acetate than in water. Since a more concentrated solution of the salt could be obtained in ammonium acetate than in water, this was used as a means of obtaining crystals suitable for measuring. The following procedure was followed. A 5 to 30% solution of ammonium acetate was carefully saturated with the salt at 40°. The excess salt was removed, and the saturated solution was allowed to cool very slowly (fifteen hours) down to room temperature while immersed in a large thermostat. This produced many small, but extremely perfect, deep ruby-red crystals. The crystals were always distorted when the concentration of the ammonium acetate was above 30 to 40%. The composition of the recrystallized and precipitated salt was found to be the same on analysis, showing that the treatment with ammonium acetate did not alter the composition of the salt.

2. **Oxalato Tetrammine Cobalti Chromate.**—All attempts to prepare this salt by the direct action of potassium chromate upon oxalato sulfate failed, but a small amount of acetic acid present caused the slow formation of the dichromate. When a small amount of ammonium carbonate was present no reaction occurred, and on evaporation the reactants were deposited unchanged. It was found that when the orange-red oxalato dichromate was boiled with ammonium carbonate it was transformed to a salt of a more nearly pure red color. An excess of the oxalato dichromate was then boiled with ammonium carbonate, and the salt, after boiling, was filtered off and used to saturate a 5 to 10% solution of ammonium carbonate at 40°. By slowly cooling this solution as described above, perfect deep red crystals were obtained which proved to be the oxalato chromate. Therefore even though the chromate cannot be made directly, it can be obtained by crystallizing the dichromate from ammonium carbonate.

⁴ Schramm, *Z. anorg. Chem.*, 180, 179 (1929).



From several ammonia determinations the composition of the chromate was found to correspond to the formula written above. The ammonia required by the formula is 24.92% and the average found from four determinations was 24.94%.

3. Carbonato Tetrammine Cobalti Dichromate.—A saturated solution of potassium dichromate at 30 to 40° is added to a solution of carbonato sulfate at 60° in the presence of a little ammonium acetate. The mixture is stirred vigorously under running water, cooled quickly and filtered at once. The filtrate after removing the precipitate, and frequently even before, turns very dark brown in color, and on standing deposits crystals of similar color. These crystals could not be obtained pure for analysis. If the carbonato sulfate solution is not completely saturated, and if the potassium dichromate solution is much above 40° and also unsaturated, no precipitate will form, but the solution turns at once dark brown in color. The bright red salt changes to this dark brown substance on standing in water solution, acetic acid, ammonium acetate, potassium and ammonium dichromate, and most attempts to recrystallize it formed this brown solution.

Constituent	Composition $\left[\text{Co}(\text{NH}_3)_4 \right]_2 \text{Cr}_2\text{O}_7$	
	Calcd., %	Found, %
Cr	17.62	17.63
NH ₃	23.08	23.00
Co	19.98	20.79
CO ₃	Not determined	

The carbonato dichromate could not be crystallized, since all solutions of the salt change in composition before crystals form.

4. Carbonato Tetrammine Cobalti Chromate.—A solution of ammonium carbonate of almost any strength is saturated with the carbonato dichromate at 30 to 40° and allowed to stand. Large individual crystals deposit on cooling which are deep red in color.

Constituent	Composition $\left[\text{Co}(\text{NH}_3)_4 \right]_2 \text{CrO}_4 \cdot \text{H}_2\text{O}$	
	Calcd., %	Found, %
Cr	10.23	10.17
NH ₃	26.81	26.76
Co	23.21	23.98
H ₂ O	3.54	3.45
CO ₃	Not determined	

As in the oxalato series the chromate could not be prepared directly, but was obtained by crystallizing the dichromate from ammonium carbonate.

5. Oxalato Tetrammine Cobalti Chlorate.—This salt, not previously described, was prepared in order to study the crystalline form of a compound containing the oxalato cation combined with a univalent anion. Oxalato sulfate was treated with the calculated quantity of barium chlorate, the barium sulfate was filtered out, and the oxalato chlorate crystallized from the filtrate in measurable crystals after several days. The cobalt found in these crystals was 19.92%, and the cobalt required by the formula is

$$19.83\% \left[\text{Co}(\text{NH}_3)_4 \right] \text{ClO}_3.$$

6. **Oxalato Tetrammine Cobalti Perchlorate.**—This salt was prepared by Brönsted, and used by him in his studies on solubility. It forms readily on mixing saturated solutions of ammonium perchlorate and oxalato sulfate. Measurable crystals were obtained

by slowly cooling an aqueous solution of the salt: $\left[\overset{\text{C}_2\text{O}_4}{\text{Co}(\text{NH}_3)_4} \right] \text{ClO}_4 \cdot \text{H}_2\text{O}$. Cobalt found, 17.78%; calcd., 17.74%.

7. **Carbonato Tetrammine Cobalti Perchlorate.**—This salt was prepared by mixing solutions of ammonium perchlorate and oxalato sulfate. The crystals were more difficult to obtain in measurable form, but were not investigated since other salts in this series could not be crystallized. $\left[\overset{\text{CO}_3}{\text{Co}(\text{NH}_3)_4} \right] \text{ClO}_4$: Cobalt found, 20.69%; calcd., 20.59%.

Remarks on the Oxalato Tetrammine Ion

Solutions of salts containing a complexly bound acido group usually undergo hydrolysis, whereby a water molecule is exchanged for the acido group. The oxalato and the carbonato tetrammine ions show a marked difference in this respect. The carbonato dichromate changes to the diaquo compound rapidly, but the chromate ions which are produced in the hydrolysis of the dichromate group immediately replace the water molecules from the complex, so that the result of the hydrolysis of the unstable carbonato group is the formation of a chromato complex compound, which is the cause of the dark brown solutions previously mentioned. Briggs⁵ has prepared compounds of this series by reactions involving the replacement of water by the CrO_4^{--} group.

Oxalato dichromate is very different from the carbonato dichromate, and hydrolyzes, producing the brown chromato compound only to a small extent after several days. Lamb has shown that the carbonato tetrammine base is as highly ionized as the alkali bases.⁶ The presence of the carbonato ion in solution appears to favor the formation of hydroxyl ions, which in turn produces a high concentration of chromate ions when the carbonato dichromate is dissolved in water. These chromate ions either replace the CO_3 directly or replace the water molecule which had previously replaced the CO_3 group. Lamb did not determine the strength of the oxalato tetrammine base, so that we can make no prediction as to whether the oxalato tetrammine ion will favor hydroxyl-ion formation. From the behavior of oxalato dichromate solutions, it appears that very few chromate ions are formed. This would indicate that the oxalato ion favors hydrogen-ion formation. Solutions of oxalato dichromate do not change to the chromato compound, either because of the failure of the oxalato group to be replaced by water, or because the oxalato complex prevents the formation of chromate ions from the dichromate group. In the event that the aquo compound is formed there is no evidence that the dichromate group becomes com-

⁵ Briggs, *J. Chem. Soc.*, 115, 67 (1919); 685 (1929).

⁶ Lamb and Yngve, *THIS JOURNAL*, 43, 2352 (1921).

plexly bound as does the chromate group. Rây and Sarkar have described a compound which contains a complexly bound Cr_2O_7 group, but this has a very complex structure and is not comparable to the type of compounds considered here.⁷

Solubility of the Salts in Water

The solubility was determined by the same method used by Brönsted.⁸

Cobalt tetrammines	Solubility at 25° G. of salt per 100 cc. of satd. soln.	Specific gravity at 25°
Oxalato sulfate	0.7712
Oxalato dichromate	.0734	2.0995
Oxalato chromate	.3156	1.9790
Oxalato perchlorate	.4403 (At 20°, Brönsted)
Carbonato sulfate	6.061
Carbonato dichromate	Decompose rapidly in water and could not be determined	2.0300
Carbonato chromate		2.0135

The composition of the salts was ascertained by determining the constituents in the following way. Chromium was determined by the lead chromate method, ammonia by the method of Brönsted, and cobalt by the nitroso beta naphthol method, not igniting the precipitate in hydrogen.

Crystallography

Crystals of the compounds studied were obtained suitable for measuring by methods already mentioned. They were, as desired, very small and did not exceed 0.1 to 0.2 mm. in their greatest dimension. A crystal which was typical of the compound was selected and accurately sketched. This sketch was used to make the final drawing from the measured angles, so that each drawing would be a faithful portrait of the compound and not a drawing of the ideal form. A small piece of wax, fastened on a spindle, was drawn out to a thin thread, which was then attached to a suitable point on the crystal. The crystal when mounted on the wax was placed on a Goldschmidt two-circle goniometer and measured with a prominent zone vertical.

The average values from the measurement of a number of crystals were used to calculate the crystallographic elements. These elements and symbols were calculated by the method of Victor Goldschmidt from a gnomonic projection.⁹ Care was taken to select the unit face so that

⁷ Rây and Sarkar, *J. Indian Chem. Soc.*, 1, 289 (1925).

⁸ J. N. Brönsted and Agnes Petersen, *THIS JOURNAL*, 43, 2265 (1921).

⁹ A series of papers edited by Edgar T. Wherry and Charles Palache describes these calculations and covers the important bibliography of the subject [*Am. Mineral.*, 5, Nos. 2-12 (1920)].

similar faces on different compounds would have similar indices, and so that the orientation of the various crystals would be comparable. The same plan was followed in assigning letters to the faces.

The crystal tables which follow contain the measurements, calculations and results of the compounds studied. The figures are reproductions of drawings made from the gnomonic projections of the average values obtained, and are in all cases real portraits and not drawings of the ideal crystal, as Victor Goldschmidt insists is the best procedure.

CRYSTAL TABLE NO. I

OXALATO TETRAMMINE COBALTI DICHROMATE

Measurement of a typical crystal, see Figs. 2 and 3

No. Let.	Symbols		Measured		Orientated		Calcd. φ	Av. top and bot.	
	G.	M.	H	V	$V - V_0$	$H - H_0$		φ	ρ
	$\left[\text{Co}(\text{NH}_3)_4 \right]_2 \text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$, Monoclinic.						$H_0 = 144^\circ 16'$		
							$V_0 = 34^\circ 56'$		
1	c	0 001	141°44'	124°56'	90°00'	2°32'	90°00'	89°59'	2°35'
4	p	$\frac{1}{2}$ 112	186 29	176 29	143 33	42 13	38 27	38 26	42 42
5	p	$\frac{1}{2}$ 112	186 57	73 20	38 14	42 41	38 14	38 26	42 42
17	\bar{e}	$\bar{1}01$	190 54	305 27	270 31	46 38	$\bar{9}0$ 31	$\bar{9}0$ 31	46 38
2	f	01 011	199 44	213 16	178 20	55 28	1 40	1 47	55 33
3	f	01 011	199 45	36 58	2 02	55 29	2 02	1 47	55 33
16	g	1 111	205 31	72 23	37 27	61 15	37 27	37 45	61 11
14	\bar{h}	$\bar{2}0$	209 01	305 06	270 10	65 45	$\bar{9}0$ 10	$\bar{9}0$ 10	64 45
15	h	20	209 44	125 01	90 05	65 28	90 05	90 01	65 25
8	b	0 ∞	010	234 21	214 54	179 58	0 02	00 00	89 58
12	b	0 ∞	010	234 16	35 09	0 13	90 00	00 00	89 58
7	m	∞ 1 110	234 03	251 11	216 15	89 47	36 15	36 36	89 58
9	m	∞ 1 110	234 18	178 25	143 29	90 02	36 31	36 36	89 58
11	m	∞ 1 110	234 20	70 56	36 00	90 04	36 00	36 36	89 58
13	m	∞ 1 110	234 14	357 57	323 01	89 58	36 59	36 36	89 58
6	a	∞ 0 100	234 00	305 00	270 04	89 44	90 04	90 01	89 58
10	a	∞ 0 100	234 19	124 58	90 02	90 03	90 02	90 01	89 58

CRYSTAL TABLE NO. II

OXALATO TETRAMMINE COBALTI DICHROMATE

Results and table of forms

$\left[\text{Co}(\text{NH}_3)_4 \right]_2 \text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$, Monoclinic				142 of the best faces from 10 crystals averaged			
Form	Symbol, M	Angles		Form	Symbol, M	Angles	
		φ	ρ			φ	ρ
c	001	90°00'	2°35'	h	201	90°00'	65°35'
p	112	38 40	42 43	\bar{h}	$\bar{2}01$	$\bar{9}0$ 00	64 45
\bar{e}	$\bar{1}01$	$\bar{9}0$ 07	46 35	b	010	00 00	89 56
f	011	1 44	55 34	m	110	36 32	89 58
g	111	37 27	61 27	a	100	90 06	90 00

Forms (p), (f) and (\bar{h}) uniformly excellent and used to calculate p_0 and q_0 .

CRYSTAL TABLE NO. II (Concluded)

POLAR ELEMENTS

$\epsilon' = 0.04512$	$h_0 = 1.0000$	$q_0 = 1.4484$
$p'_0 = 1.0683$	$\epsilon = 0.04507$	$r_0 = 1.0000$
$q'_0 = 1.4499$	$p_0 = 1.0672$	$\mu = 87^\circ 25'$

LINEAR ELEMENTS

$$a : b : c \qquad \beta = 92^\circ 35'$$

$$1.3586:1:1.4484$$

The legend used is the usual one of Goldschmidt. (ρ) is the angle of the face normal from the vertical pole or may be thought of as the co-latitude (φ) is the angle from a suitable horizontal meridian, and may be thought of as the longitude.

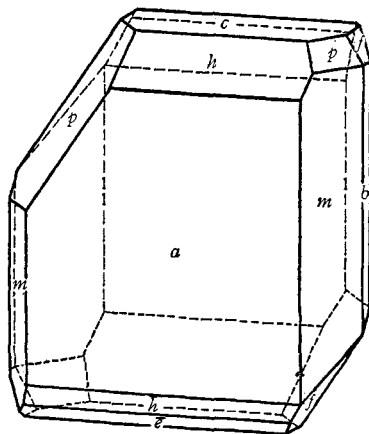
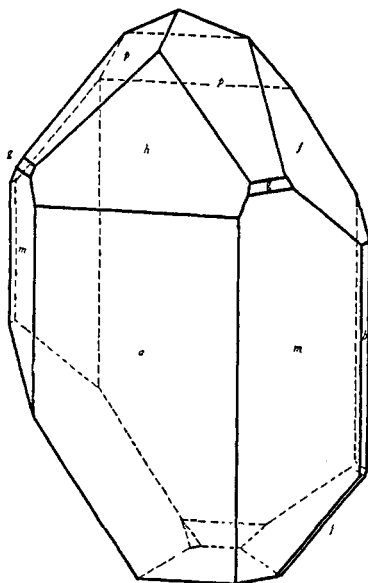
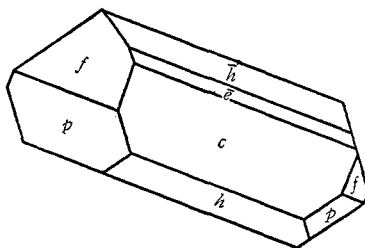
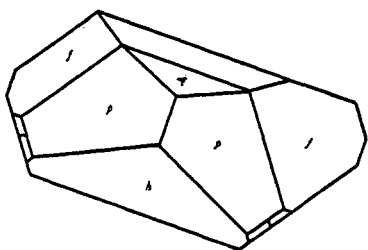


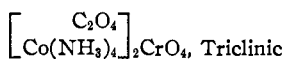
Fig. 2.—Oxalato tetrammine cobalti dichromate, monoclinic (hemihedral habit).

Fig. 3.—Oxalato tetrammine cobalti dichromate, monoclinic (regular habit).

CRYSTAL TABLE NO. III

OXALATO TETRAMMINE COBALTI CHROMATE

Measurement of a typical crystal, see Fig. 4



$$H_0 = 144^\circ 14'$$

 $V_0 = (\text{see below})$

No.	Let.	Symbols		Measured			Av. angles from 12 crystals	
		G.	M.	H	V	V - V ₀	(φ)	(ρ)
1	c	0	001	176°18'	43°48'	89°40'	89°40'	32°25'
2	Ö	$\frac{1}{2}\bar{1}$	$\bar{1}\bar{2}1$	188 17	136 37	182 14	$\bar{2}$ 14	44 25
3	h	20	201	Not on this crystal			90 05	73 23
7	0	$\frac{1}{2}\bar{1}$	$\bar{1}\bar{2}1$	185 25	313 13	357 58	$\bar{1}\bar{7}\bar{7}$ 58	44 45
20	ē	$\bar{1}0$	$\bar{1}01$	179 24	224 26	270 40	$\bar{9}0$ 40	35 12
4	M	$\infty\bar{1}$	$\bar{1}\bar{1}0$	234 10	100 38	146 00	146 00	90 00
5	a	$\infty 0$	100	234 30	44 23	90 15	90 15	90 00
6	m	$\infty 1$	110	234 13	348 50	34 19	34 19	90 00
8	M	$\infty\bar{1}$	$\bar{1}\bar{1}0$	234 10	281 00	326 00	146 00	90 00
9	a	$\infty 0$	100	234 28	224 18	270 15	90 15	90 00
10	m	$\infty 1$	110	234 15	167 07	214 19	34 19	90 00

No actual values for V_0 were obtained, but the (V) values were orientated by getting the best average angle between like faces from twelve different crystals. Face (5) was then set at 90° and from the angles obtained all other faces were orientated with respect to this one. The plot of these values (V') showed that it was necessary to move all these values clockwise $0.15'$ in order that zone (0-01) be parallel to the horizontal meridian. This gave at once the necessary known terms to calculate the polar elements. This procedure was necessary because no (010) face was present on any of the crystals examined. Even though these crystals appeared to be very brilliant, they gave many blurred and ghost signals. For this reason the calculations were made entirely from averaged values. The compound was at first thought to be monoclinic, and faces 5, 1, 3, 20 and 9 to be in the plane of symmetry. Because of the blurred signals the variation of the measurements from monoclinic values were within the limit of reading error. That the crystal was triclinic was demonstrated by examining it with polarized light. With crossed nicols an extinction angle of 8° was obtained for all faces whose face poles were parallel with the supposed symmetry plane. Hence the measurements were averaged and calculated as triclinic. The symmetry of the crystal is very close to monoclinic since angles alpha and gamma are near 90° .

A special form table for the oxalato chromate is not included, since almost each face is a separate form. The last two columns of Table III give the average angles from the measurement of twelve different crystals instead of the angles from one typical crystal for, as mentioned above, the signals from many of the faces were so poor that the calculations had to be made solely from average values. Reference to Fig. 4 will show the prominence of the forms. The results are listed below.

POLAR ELEMENTS

$x'_0 = 0.6350$	$x_0 = 0.53607$	$v = 90^\circ 15'$
$y'_0 = 0.00203$	$y_0 = 0.00172$	$\lambda = 89^\circ 54'$
$p'_0 = 1.3434$	$p_0 = 1.1341$	$\mu = 57^\circ 35'$
$q'_0 = 0.9864$	$q_0 = 0.8326$	$\varphi_0 = 89^\circ 45'$
$h_0 = 1.0000$	$r_0 = 1.0000$	$\rho_0 = 32^\circ 25'$

LINEAR ELEMENTS

$a : b : c$	$\alpha = 90^\circ 16'$	$\gamma = 89^\circ 30'$
1.5767 : 1 : 1.3434	$\beta = 122^\circ 26'$	

CRYSTAL TABLE NO. IV

OXALATO TETRAMMINE COBALTI CHLORATE

Measurement of a typical crystal, see Fig. 5

		C_2O_4				$H_0 = 00^\circ 00'$			
		$[Co(NH_3)_4]ClO_3$, Triclinic				$V_0 = 148^\circ 07'$			
No.	Let.	Symbol G.	M.	Measured H V		Orientated $V - V_0$	Calculated φ		ρ
1	b	0	010	90°00'	328°07'	180°00'	0°00'	90°00'	
2	n	$\bar{1}\bar{1}$	$\bar{1}\bar{1}0$	90 00	291 44	142 37	142 37	90 00	
3	t	$\infty 1\frac{1}{2}$	$2\bar{1}0$	90 00	273 11	125 04	125 04	90 00	
4	a	$\infty 0$	100	90 00	238 11	90 04	90 04	90 00	
5	r	$\infty 1\frac{1}{2}$	210	90 00	203 05	55 28	55 28	90 00	
6	m	$\infty 1$	110	90 00	185 03	36 56	35 56	90 00	
7	n	$\infty \bar{1}\bar{1}$	$\bar{1}\bar{1}0$	90 00	111 46	323 39	142 39	90 00	
8	t	$\infty \bar{1}\frac{1}{2}$	$2\bar{1}0$	90 00	92 41	304 34	124 34	90 00	
9	a	$\infty 0$	100	90 00	57 49	269 42	89 42	90 00	
10	r	$\infty 1\frac{1}{2}$	210	90 00	23 37	235 30	55 30	90 00	
11	m	$\infty 1$	110	90 00	4 29	216 20	36 22	90 00	
12	\bar{P}	$\frac{1}{2}$	$\bar{1}\bar{1}2$	41 36	359 48	211 41	$\bar{3}1$ 41	41 36	
13	P	$\frac{1}{2}$	$\bar{1}12$	42 02	115 44	327 37	$\bar{1}47$ 35	42 02	
14	c	0	001	4 58	236 01	87 54	87 54	4 58	

CRYSTAL TABLE NO. V

OXALATO TETRAMMINE COBALTI CHLORATE

Results and table of forms

		C_2O_4				Average of 80 best faces from six crystals			
		$[Co(NH_3)_4]ClO_3$, Triclinic				Angles			
Form	Symbol, M	φ	ρ	Form	Symbol, M	φ	ρ	Form	Symbol, M
a	100	89°58'	90°00'	r	210	55°34'	90°00'		
b	010	00 00	90 00	t	$2\bar{1}0$	124 29	90 00		
c	001	87 45	4 58	\bar{P}	$\bar{1}\bar{1}1$	$\bar{3}1$ 46	41 36		
m	110	36 52	90 00	P	$\bar{1}\bar{1}1$	$\bar{1}47$ 35	42 08		
n	$\bar{1}\bar{1}0$	143 20	90 00						

POLAR ELEMENTS

$x'_0 = 0.08683$	$p'_0 = 1.1260$	$(\varphi_0) = 87^\circ 45'$
$y'_0 = 0.00341$	$q'_0 = 1.5185$	$(\rho_0) = 4^\circ 58'$
$x_0 = 0.08651$	$p_0 = 1.1218$	$(\lambda) = 89^\circ 48'$
$y_0 = 0.00340$	$q_0 = 1.5128$	$(\mu) = 85^\circ 02'$
$h_0 = 1.0000$	$r_0 = 1.0000$	$(\nu) = 89^\circ 58'$

CRYSTAL TABLE NO. V (Concluded)

LINEAR ELEMENTS

$$a : b : c \\ 1.3536 : 1 : 1.5185$$

$$(\alpha) = 90^{\circ}12' \quad (\gamma) = 79^{\circ}26' \\ (\beta) = 98^{\circ}52'$$

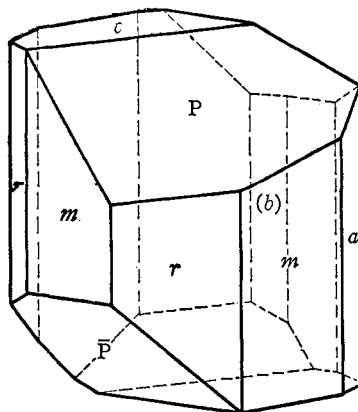
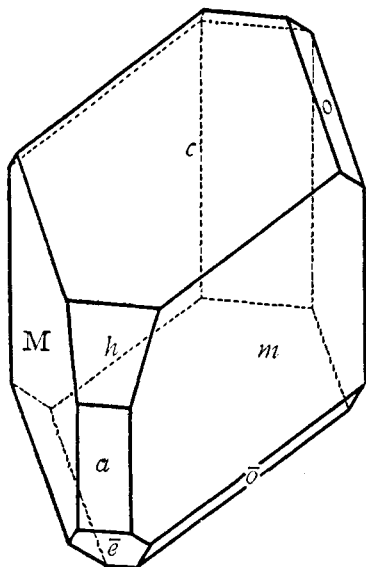
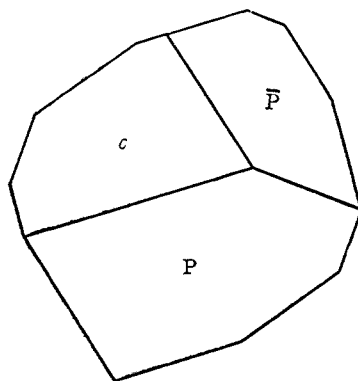
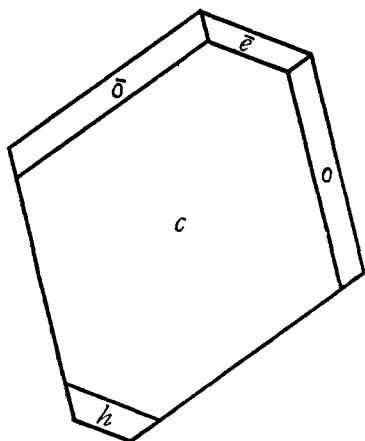


Fig. 4.—Oxalato tetrammine cobalt¹ chromate, triclinic.

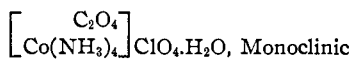
Fig. 5.—Oxalato tetrammine cobalti chlorate, triclinic (drawn with b front).

CRYSTAL TABLE NO. VI

OXALATO TETRAMMINE COBALTI PERCHLORATE

Results and table of forms

The number of forms developed on this compound is so small that all the necessary data can be included in one table.



Form	Symbol, M	Angles		Form	Symbol, M	Angles	
		φ	ρ			φ	ρ
a	100	90°00'	90°00'	\bar{e}	201	90°00'	38°06'
b	010	00 00	90 00	m	110	33 26	90 00
c	001	90 00	9 58	r	210	52 45	90 00
d	012	13 15	35 57				

See Fig. 6 for face development.

POLAR ELEMENTS

ϵ'	= 0.1740	ϵ	= 0.1714		
p'_0	= 0.4791	p_0	= 0.4719	μ	= 80°02'
q'_0	= 1.4634	q_0	= 1.4414		
h_0	= 1.0000	r_0	= 1.0000		

LINEAR ELEMENTS

$$a : b : c \qquad \beta = 99^\circ 58'$$

$$1.5508 : 1 : 1.4634$$

CRYSTAL TABLE NO. VII

CARBONATO TETRAMMINE COBALTI CHROMATE

Measurement of a typical crystal, see Fig. 7



$$H_0 = 234^\circ 10'$$

$$V_0 = (\text{see below})$$

No.	Let.	Symbol		Measured		Orientated		Calculated	
		G.	M.	H	V	V ⁻	V ⁺	φ	ρ
1(18)	c	0	001	165°17'	3°50'	91°38'	88°22'	88°22'	21°07'
2(17)	e	10	101	204 16	3 39	91 27	88 33	88 33	60 04
3(16)	\bar{e}	10	$\bar{1}01$	188 54	185 05	271 12	268 48	88 48	44 23
4	G	$\bar{1}$	$\bar{1}11$	201 00	132 16	219 30	320 30	140 30	56 58
6(13)	\bar{f}	0	$\bar{1}1$	195 49	230 35	17 46	162 14	162 14	51 31
20(15)	\bar{P}	$\frac{1}{2}$	$\bar{1}\bar{1}2$	178 36	246 37	357 07	205 53	25 53	34 23
21(14)	\bar{G}	$\bar{1}$	$\bar{1}\bar{1}1$	201 46	234 18	321 53	218 07	38 07	57 45
7	b	0 ∞	010	234 23	92 07	180 00	0 00	00 00	90 00
8	m	$\infty 1$	110	234 13	44 48	132 33	47 27	47 27	90 00
9	M	$\infty \bar{1}$	$\bar{1}\bar{1}0$	234 17	321 38	49 16	130 44	130 44	90 00
10	b	0 ∞	010	234 08	272 22	00 00	180 00	00 00	90 00
11	m	$\infty 1$	110	234 11	225 00	312 33	227 27	47 27	90 00
12	M	$\infty \bar{1}$	$\bar{1}\bar{1}0$	234 05	140 35	229 16	310 44	130 44	90 00
19	a	$\infty 0$	100	234 10	182 51	91 20	88 40	88 40	90 00
22	a	$\infty 0$	100	234 57	3 33	271 20	268 40	88 40	90 00

The ordinary methods for determining (V_0) could not be employed here. After plotting, faces (7) and (10) were found to be (010) and when correctly rotated should have a (φ) angle of zero and be at zero on the projection. The angles between all forms measured were determined and the

values in each case averaged. By this means the best average angle between that form and (010) was found. This gave a set of vertical readings which

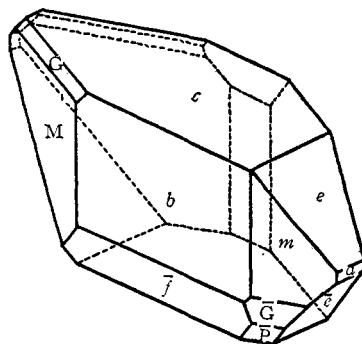
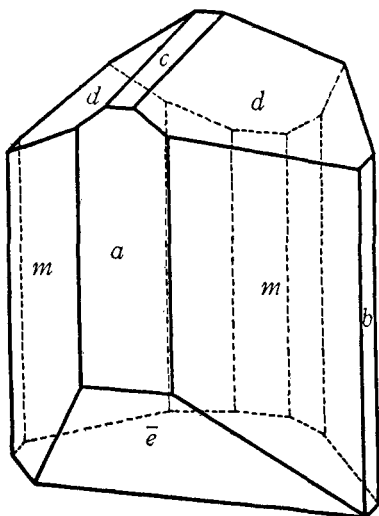
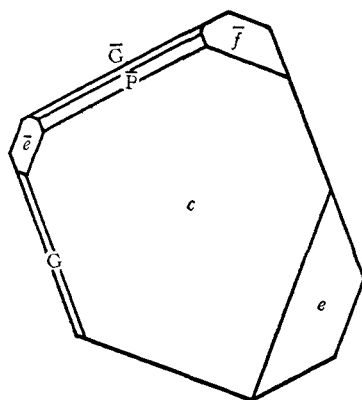
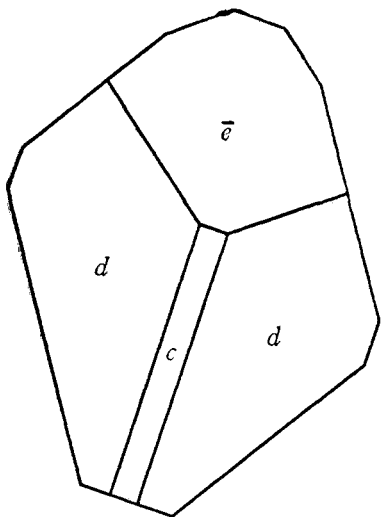


Fig. 6.—Oxalato tetrammine cobalti perchlorate, monoclinic.

Fig. 7.—Carbonato tetrammine cobalti chromate, triclinic (drawn with b front).

are recorded in column (V^-) of Table VII. By examining the plot it was found that the negative end of the crystal had been measured and sketched. The (V^-) values, therefore, were adjusted to their complementary position.

The values in column (V^+) are the results of this readjustment, and from them the (φ) values were calculated.

CRYSTAL TABLE NO. VIII
CARBONATO TETRAMMINE COBALTII CHROMATE
Results and table of forms

Form	Symbol, M	Angles		Form	M	Angles	
		φ	ρ			φ	ρ
a	100	88°40'	90°00'	\bar{G}	$\bar{1}\bar{1}\bar{1}$	38°07'	57°45'
b	010	00 00	90 00	\bar{f}	0 $\bar{1}\bar{1}$	162 41	51 31
c	001	88 22	21 07	\bar{P}	$\bar{1}\bar{1}\bar{2}$	25 53	34 23
e	101	88 33	60 04	m	110	47 27	90 00
\bar{e}	$\bar{1}01$	88 48	44 23	M	110	130 44	90 00
G	$\bar{1}\bar{1}\bar{1}$	$\bar{1}40$ 30	56 58	See figure for development of forms.			

POLAR ELEMENTS

$x'_0 = 0.3718$	$p'_0 = 1.3497$	$(\varphi_0) = 88^\circ 22'$
$y'_0 = 0.0104$	$q'_0 = 1.2060$	$(\rho_0) = 21^\circ 07'$
$x_0 = 0.3632$	$p_0 = 1.2592$	$(\tau) = 89^\circ 27'$
$y_0 = 0.00967$	$q_0 = 1.1250$	$(\mu) = 68^\circ 42'$
$h_0 = 1.0000$	$r_0 = 1.0000$	$(\nu) = 88^\circ 40'$

LINEAR ELEMENTS

$a : b : c$	$(\alpha) = 90^\circ 05'$	$(\gamma) = 91^\circ 14'$
0.9589 : 1 : 1.5197	$(\beta) = 111^\circ 17'$	

Conclusions

As anticipated, the crystalline form and habit of a compound was affected as one of the groups was substituted. It appears that the structural type of all the oxalato tetramine compounds studied is the same, because the symmetry of their crystalline forms bear simple relations to one another. If this is correct, then the deforming influence of the substituted anions upon the structure of the oxalato group may be stated as having the following increasing order: Cr_2O_7 , ClO_4 , ClO_3 and CrO_4 .

From infra-red absorption data, Rawlins¹⁰ has suggested that in compounds of the type ABX, the AB portion of the compound may preserve a well-defined skeleton structure in various compounds as various atoms or groups are substituted for the X portion. Similarly, the oxalato tetramines described in this paper may be given a type formula as follows—AXY. In the compounds described by Rawlins the two cations preserve a definite structure in various combinations. In the oxalato complexes, or in any acido ammonia complex, it is entirely possible that the AX portion of the molecule preserves a definite skeleton structure which is merely altered or deformed as various substitutions of (Y) are performed. This is merely another definition of a complex ion, and states that two atoms or groups which under some conditions exist as a single anion and cation are now combined in some way so that the combination acts as a definite new ion.

¹⁰ Rawlins, *Trans. Faraday Soc.*, 25 283 (1929).

Complex ions are usually considered in the same way as more simple ions, *i. e.*, to be more or less spherical. Pauling¹¹ has discussed the ionic radii of a few complex ions and their radius ratios. There is no literature which is opposed to assigning a definite skeleton structure to a complex ion of the type AX^+ , and indeed such a structure appears to exist. Quantitative verification of the exact effect of the substituted anion in these oxalato complexes will be possible only after an x-ray determination of their structural types and cell dimensions. If the structural type is not altered by the substitution of the anion, then, as stated in the introduction, the axial ratios of a series of compounds which contain a complex ion will be adequate to measure the effect produced by the substituted anion.

Summary

1. The following new compounds have been prepared and analyzed: the chromate, dichromate and chlorate of the oxalato tetrammine series of cobalt, also the chromate and dichromate of the carbonato series.

2. Crystals of all the above compounds, except the carbonato dichromate have been prepared. These crystals, in addition to the oxalato perchlorate, were measured and the crystalline forms determined.

3. The difficulty encountered in preparing the oxalato chromate suggests an interesting example of the manner in which affinity of ions for each other may limit their deforming influence.

4. It is suggested that the complex oxalato cobalti tetrammine ion, and other acido complexes, may have a definite skeleton structure in crystals containing this complex ion, and that the substitution of various anions merely alters the shape and dimensions of this structure.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]
**A PERIODIC ARRANGEMENT OF THE ATOMIC NUCLEI. THE
PREDICTION OF ISOTOPES**

BY HERRICK L. JOHNSTON

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Interesting and suggestive regularities in the existence and abundance of mass numbers have been called to attention by various authors in recent years.¹ The most thorough tabulations of such empirical regularities are those of Harkins. The discovery of such relationships is useful not only in

¹¹ L. Pauling, *THIS JOURNAL*, **49**, 765 (1927).

¹ (a) Harkins, *ibid.*, **39**, 859 (1917); **42**, 1976 (1920); **43**, 1050 (1921); **45**, 1426 (1923); *Phil. Mag.*, **42**, 331 (1921); *Phys. Rev.*, **15**, 85 (1920); *J. Franklin Institute*, **195**, 554 (1923); *Chem. Reviews*, **5**, 371 (1928); (b) Beck, *Z. Physik*, **47**, 407 (1928); (c) Barton, *Phys. Rev.*, **35**, 408 (1930); (d) Latimer, *THIS JOURNAL*, **53**, 981 (1931).