linkage, the maximum quantity of bound copper serves to balance the free carboxyl groups in the expected ratio of 1:2.

A few spectrophotometric experiments were also carried out with 0.01 *M* copper in aqueous 0.1 *M* NaCl solutions of synthetic polylysine at a *p*H of 4.9. The spectra obtained could not be distinguished from those of copper chloride in 0.1 *M* NaCl aqueous solution. In this respect polylysine behaved like lysozyme. Evidently the large positive charge on the polypeptide molecule produces such a strong repulsion toward Cu^{++} ions that even at a concentration of 1×10^{-2} *M* they are unable to compete effectively with 1×10^{-4} *M* hydrogen ions for the amine groups.

Conclusions.—In contrast to protein interactions with anions, the interactions described in the present paper indicate no unique affinity characteristic of any one of the proteins examined. Binding of cupric ions thus seems to be more nearly analogous to uptake of hydrogen ions by proteins. The requirements for binding seem to be primarily the presence of appropriate residues and favorable electrostatic conditions in the macromolecule.

Acknowledgment.—This investigation was supported by grants from the Carnation Company. We are indebted especially to Dr. E. B. Oberg and Mr. W. C. Cross for their interest.

EVANSTON, ILLINOIS RECEIVED JUNE 8, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF WASHINGTON]

Structural Properties of Chromium(III) Iodide and Some Chromium(III) Mixed Halides

BY L. L. HANDY AND N. W. GREGORY

Powder patterns indicate that chromium(III) iodide is isostructural with chromium(III) chloride, with hexagonal unit cell parameters $a = 6.86$ and $c = 19.88$. The three mixed halides $CrICl_2$, $CrIBr_2$ and $CrBrCl_2$, formed by reaction of the less active halogen with the corresponding chromium(II) salt, appear structurally equivalent to that expected for an ideal solid solution of CrX_3 and CrY_3, with the exception that the halide layers are not as closely packed.

The crystal structures of anhydrous chromium(III) iodide and of some chromium(III) mixed halides ($CrICl_2$, $CrIBr_2$ and $CrBrCl_2$) have been investigated. The products indicated by the formulas $CrXY_2$ were formed by reaction of the less active halogen X_2 with the chromium(II) salt CrY_2. The structural relationship of the mixed and simple halides was of particular interest. A report of some thermodynamic properties of these substances will be made in a forthcoming paper.

The structures of the chromium(III) halides are sufficiently similar to permit indexing of powder patterns from the known characteristics of $CrCl_3$ and $CrBr_3$. Wooster[1] has made a detailed study of the anhydrous chromium(III) chloride structure. It has been assigned the space group $D_3^3(H3_12)$-D_3^5 $(H3_22)$ with $a = 6.02$ Å. and $c = 17.3$ Å. Braekken[2] found $CrBr_3$ to have a very similar structure with slightly different space group, C_3^1 (C3) or C_{3i}^1 $(C\overline{3})$ with $a = 6.26$ Å. and $c = 18.2$ Å. A large group of metallic halides with formula MX_3 crystallize with the latter arrangement, frequently called the BiI_3 structure, but the $CrCl_3$ arrangement has not hitherto been found among other compounds of this type. Both structures consist of a double-layer lattice of halogen atoms based on a closest packing arrangement (cubic in $CrCl_3$ and hexagonal in $CrBr_3$). Chromium atoms in a regular hexagonal arrangement occupy two-thirds of the octahedral interstices within the double layers, but different double layers are apparently held together by van der Waals forces only.

The structure factors are such as to permit an easy distinction between the two types: diffraction lines from the 112, 114, 118, etc., are characteristic of $CrCl_3$, whereas 113, 116, 119, etc., appear from $CrBr_3$. In the present work the powder patterns of CrI_3 and of the mixed halides prepared by halogen oxidation correspond to the $CrCl_3$ structure.

Experimental Part

Powder patterns were taken with samples in sealed thin walled Pyrex capillary tubes approximately 0.6 mm. in diameter. The sample tubes were prepared in a dry-box. Exposures were made for 24- to 36-hour period, using copper radiation filtered with nickel. Several samples from independent preparations of each material were used with satisfactory agreement of spacings observed on each. The values reported were taken from the best pattern in each case.

The preparation of CrI_3 has been described in an earlier paper.[3] Anhydrous $CrBr_3$ and $CrCl_3$ were prepared by standard methods and purified by sublimation under high vacuum in quartz. The mixed halides $CrIBr_2$ and $CrICl_2$ were prepared by reaction of iodine with $CrBr_2$ and $CrCl_2$, respectively, in a manner analogous to that described for iodination of CrI_2.[3] The decomposition pressure of iodine above these substances becomes quite large before the vapor pressure is sufficiently high to effect sublimation. The reaction of iodine with the chromium(II) salts was observed to be reversible.

$CrBrCl_2$ was prepared in a similar manner by bromination of $CrCl_2$. Other mixtures of varying composition in the $CrCl_3$–$CrBr_3$ system were prepared by heating predetermined amounts of $CrCl_3$ and $CrBr_3$ in high vacuum until sublimation occurred (≈ 700°). On condensation of the vapor a homogeneous product was obtained.

Analyses.—The treatment necessary to dissolve anhydrous chromium(III) halides makes good halogen determinations difficult. On ignition in air these compounds liberate halogen and form Cr_2O_3. This has been found satisfactory as a method of determining halogen content by weight loss. The oxide may be fused with sodium peroxide and the chromium content confirmed by standard analytical methods.

Since either oxide impurity or an excess of chromium(II) salt from incomplete reaction would make the chromium percentage appreciably higher than the theoretical value expected for the mixed halide, it was considered sufficient

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(1) Nora Wooster, *Z. Krist.*, **74**, 363 (1930).

(2) H. Braekken, *Kgl. Norski. Videnskab. Selskab. Forh.*, **5**, No. 11 (1932).

(3) L. L. Handy and N. W. Gregory, THIS JOURNAL, **72**, 5049 (1950).

in most cases to use the chromium determination as a criterion of purity. Halogen content in the mixed halide samples was confirmed by dissolving the material in boiling alkaline sodium sulfite and precipitating silver halide. The weight of the latter was combined with observed weight loss on combustion to obtain the ratio of halogens. The halogen determinations made in this way were considered to have an uncertainty of several per cent.

A sample of chromium analyses for the various substances is tabulated below. Analysis of CrI_3 samples has been reported earlier.[3]

Substance	Cr(obs.), %	Cr(theor.), %
$CrIBr_2$	15.6	15.36
$CrICl_2$	21.0	20.82
$CrBrCl_2$	25.8	25.64

The composition of mixtures prepared from $CrCl_3$ and $CrBr_3$ was determined by analysis of chromium content only.

Results and Discussion

The powder pattern data for CrI_3 and the mixed halides prepared by oxidation of the chromium(II) salts are given in Table I along with the values obtained for $CrCl_3$ and $CrBr_3$ in this Laboratory. A close correspondence of the structures is apparent. The $CrBr_3$ arrangement is unique among those substances listed. It is possible, in view of the different sizes of the halogen atoms, that the mixed halides are not truly in a simple hexagonal lattice but only apparently so. Both the $CrBrCl_2$ and $CrICl_2$ patterns were found to have one diffraction line of low intensity which does not correspond to the regularities observed in $CrCl_3$. However, the close correlation of the rest of the powder data with $CrCl_3$ indicates that any deviation from this type of structure must be slight. $CrICl_2$ patterns were difficult to obtain because of the small particle size. The thermal instability of this material (loss of iodine) makes it difficult to grow crystals of appreciable size *via* the vapor phase.

The "*a*" parameters of the three $CrYX_2$ substances are in fairly close accord with that which might be expected by interpolation for a solid solution of corresponding composition of CrX_3 and CrY_3. The '*c*' dimensions are somewhat larger than would be predicted on this basis with the deviation most

TABLE I

SUMMARY OF POWDER DATA FOR CHROMIUM(III) HALIDES

	$CrBr_3$		$CrCl_3$		CrI_3		$CrBrCl_2$		$CrICl_2$		$CrIBr_2$	
hkl	d_0 (d_c)	Rel. *I*	d_0 (d_c)	Rel. *I*	d_0 (d_c)	Rel. *I*	d_0 (d_c)	Rel. *I*	d_0 (d_c)	Rel. *I*	d_0 (d_c)	Rel. *I*
003	6.152 (6.116)	4	5.804 (5.813)	8	6.605 (6.626)	2	5.943 (5.940)	10	6.252 (6.233)	7	6.371 (6.380)	4
110	3.158 (3.154)	2										
006	3.062 (3.058)	4	2.925 (2.906)	3	3.331 (3.313)	2	2.967 (2.970)	8	3.148 (3.117)	3	3.196 (3.190)	4
112	...		2.817 (2.817)	2	3.240 (3.242)	8	2.864 (2.868)	4	2.957 (2.951)	4	3.087 (3.087)	8
113	2.803 (2.803)	10	...		...		...		2.775 ?	2	...	
114	...		2.460 (2.458)	10	2.830 (2.823)	10	2.499 (2.505)	10	2.596 (2.591)	10	2.696 (2.695)	10
116	2.195 (2.196)	6	...		...		1.936 ?	2	...		...	
118	...		1.745 (1.758)	1	2.013 (2.013)	2	1.793 (1.795)	7	1.869 (1.868)	2	1.929 (1.929)	2
300	1.821 (1.821)	8	1.718 (1.719)	8	1.980 (1.980)	6	1.755 (1.749)	7	1.800 (1.800)	4	1.883 (1.883)	6
303	1.743 (1.745)	1	1.646 (1.648)	2	...		1.674 (1.678)	1				
119	1.715 (1.713)	2	...		...		...		...		...	
306	1.565 (1.565)	4			1.698 (1.700)	4	1.512 (1.507)	1			1.624 (1.622)	1
0012	1.529 (1.529)	4	1.447 (1.453)	1	1.657 (1.657)	1	1.488 (1.485)	6	1.558 (1.558)	2	1.595 (1.595)	1
224	...		1.411 (1.409)	1	1.620 (1.621)	1	1.434 (1.434)	4	1.475 (1.475)	1	1.542 (1.543)	1
226	1.403 (1.402)	1	...		...		...		...		...	
228	...				1.413 (1.412)	1	1.254 (1.252)	1				
229	1.250 (1.248)	1	...		...		...		...		...	
3012	1.172 (1.171)	5	1.106 (1.109)	1	1.268 (1.271)	1	1.136 (1.132)	3			1.222 (1.217)	1
a	6.308		5.953		6.859		6.058		6.235		6.523	
c	18.35		17.44		19.88		17.82		18.70		19.14	
Av. dev. of d_0 from p_c	0.11%		0.25%		0.16%		0.19%		0.31%		0.09%	

pronounced in the case of $CrICl_2$ and $CrIBr_2$. 'a' is effectively determined by the Cr–X (and Cr–Y) distance whereas 'c' is also dependent on the closeness of packing of the halogen layers.

The structure and composition of $CrBrCl_2$ does not change within experimental error on sublimation in high vacuum at 700°. This has been determined by comparison of powder patterns and analyses of samples subjected to successive partial sublimations (*i.e.*, only a fraction of the material was sublimed away). The powder data obtained from the product formed by direct reaction of bromine with $CrCl_2$ at 500° are rather incomplete, presumably because of small particle size. Although poor definition and low intensity made measurement of this pattern difficult, the spacings were identical (within experimental error) with those obtained after sublimation of the samples. The data in Table I were taken from a sublimed sample.

A comparison of powder patterns obtained from $CrBrCl_2$ formed by bromination of chromium(II) chloride with those of other mixtures formed by mixed sublimation of $CrCl_3$ and $CrBr_3$ suggests that all these substances are part of the same system, and that $CrBrCl_2$ is equivalent to a solid solution of $CrCl_3$ and a hypothetical $CrBr_3$ having the same structure. The cell constants observed for the mixtures are shown in Table II, and the relationship of these data to corresponding values for $CrCl_3$, $CrBrCl_2$ and $CrBr_3$ is illustrated in Fig. 1.

TABLE II

CELL DIMENSIONS OBSERVED FOR SUBLIMED MIXTURES OF $CrCl_3$ AND $CrBr_3$

Effective mole fraction bromide	"a"	"c"	Av. dev. of $d$calc. from $d$obs., %
0.55	6.149	18.08	0.26 (14 lines obsd.)
.65	6.183	18.19	.44 (10 lines obsd.)
.78	6.225	18.19	.49 (12 lines obsd.)

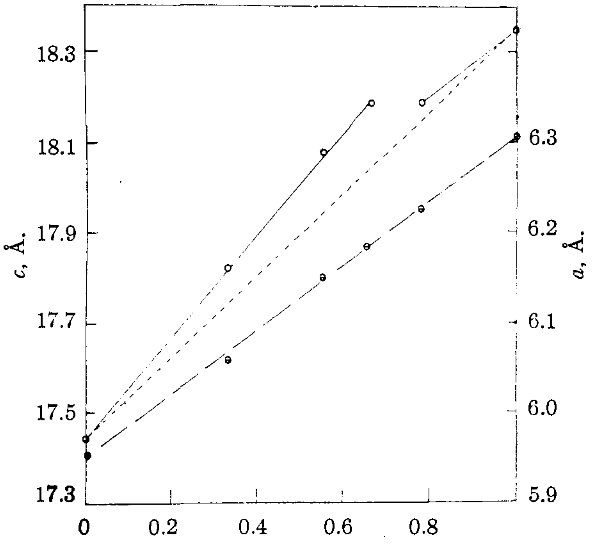

Fig. 1.—Variation of unit cell parameters with composition in the $CrCl_3$-$CrBr_3$ system: ⊖— —, a; O==, c.

It is observed from the irregularity in 'c' that the transition from the $CrCl_3$ type structure to the $CrBr_3$ structure occurs between 0.65- and 0.78-mole fraction of bromide. No irregularity appears in 'a'. It is planned to investigate this composition range in more detail to determine if this change is associated with the possible compound $CrBr_2Cl$. Thermal instability of similar mixtures involving iodine made it impractical to study the iodide systems by the sublimation technique.

There is no apparent explanation for the change in the nature of the packing of halogens in the bromide rich crystals, particularly in view of the similarity between $CrCl_3$ and CrI_3.

SEATTLE, WASHINGTON RECEIVED JULY 16, 1951

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

A Polarographic Study of the Kinetics of the Ring → Aldehydo Transformation for Various Aldoses

BY PAUL DELAHAY AND JACOB E. STRASSNER[1]

Polarographic waves of arabinose, xylose, galactose, mannose and dextrose in buffer solutions of pH 6.5 to 9.5 are studied in the 0–70° range. Limiting currents are entirely controlled by the rate of the ring → aldehydo transformation. Experimental data are interpreted quantitatively. The same energy of activation 16.5 ± 0.5 kcal. is involved in the rupture of the ring structure of all the aldoses. The entropies of activation are low (less than 10 cal. deg.$^{-1}$) and positive. An equation giving the influence of temperature on limiting currents controlled by rate of reaction and by diffusion is derived.

From their investigation of the polarographic behavior of various aldoses Heyrovsky and Smöler[2] concluded that these substances are not reduced at the dropping mercury electrode. This conclusion, however, had to be revised after Cantor and Peniston[3] obtained polarographic waves with various aldoses at concentrations of the order of 0.1 molar. Even at these relatively high concentrations only rather low limiting currents were observed. This was explained by assuming that the aldehydo form of an aldose is in equilibrium with a much larger amount of the ring form. Only the aldehydo form would be reducible and consequently low limiting currents would be observed even at high concentrations of aldose. The validity of this interpretation was already questioned by Kolthoff and Lingane[4] in 1941, and more recently it was shown by Wiesner[5] that the conclusions of Cantor and Peniston had to be modified. Wiesner observed

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[1] From a thesis to be submitted by J. E. Strassner to the Graduate School of Louisiana State University in partial fulfillment of the requirements for the degree of Master of Science.

[2] J. Heyrovsky and I. Smöler, *Collection Czechoslov. Chem. Communs.*, **4**, 521 (1932).

[3] S. M. Cantor and D. P. Peniston, THIS JOURNAL, **62**, 2113 (1940).

[4] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1941, p. 358.

[5] K. Wiesner, *Collection Czechslov, Chem. Communs.*, **12**, 64 (1947).