

is the greater the more electronegative one element is with respect to the other.

10. Electropositive groups, such as the ammonium group, are virtually metals although their stability in the free state is not sufficient to permit their isolation in most instances. The most stable groups possess sufficient stability to demonstrate their metallic properties in the free state. Such groups resemble elements in their properties.

11. *The property of metallicity is not an atomic one.* It may be imparted to non-metallic elements by combination with other non-metallic elements. *The metallic state is due to the presence of uncombined negative electrons.*

12. The electrons which impart metallic properties to an element are those to which the chemical reactions of this element with other elements are due.

13. The reaction between strongly electropositive and strongly electronegative elements or groups of elements consists essentially in a combination of the negative electrons of the electropositive constituent with the atoms of the electronegative constituent.

14. In the metal ammoniates of the type $\text{Ca}(\text{NH}_3)_6$, which are metallic substances, the negative electrons are not primarily concerned.

The detailed experimental material on which this paper is based will appear in forthcoming publications. The experimental work has been in part supported by grants from the Warren Fund of the American Academy of Arts and Sciences. I wish to acknowledge my indebtedness to these grants which have greatly facilitated the accumulation of the necessary experimental material.

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THE CRYSTAL STRUCTURES OF THE HEXAMMONIATES OF THE NICKEL HALIDES

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Introduction.—When an excess of ammonium hydroxide is added to a solution of one of the nickel halides, small octahedral crystals are precipitated. These crystals have the composition $\text{NiX}_2 \cdot 6\text{NH}_3$, where X is chlorine, bromine or iodine.

Single crystals of considerable size can be grown by slow cooling from a not too strong solution. These are rarely perfect in internal structure and all of them are extremely fragile. Because of the ease with which

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they shattered, thin sections could not be prepared and the X-ray observations had to be carried out upon entire crystals.

Microscopic examination showed these crystals to be completely isotropic. Nothing is known, however, concerning the class of the cubic system to which they should be assigned. Goniometric observations would be possible only at a low temperature, because owing to decomposition through loss of ammonia the crystal faces tarnish almost immediately after removal from the solution. The preparation of Laue photographs, which required several hours, was accomplished by imbedding the specimen in wax, thus inhibiting this decomposition.

This study of crystal structure was carried out by the aid of the generally applicable methods based upon the use of the theory of space groups which have already been described.²

The Unit Cell and the Number of Associated Molecules.—Comparison reflection photographs against a cleavage face of calcite and an octahedral face of a crystal of $\text{NiCl}_2 \cdot 6\text{NH}_3$ were prepared in the usual manner.³ Values of d_{111}/n (the ratio of the spacing of octahedral planes into the order of the spectrum) obtained from this photograph combined with the density (1.526) as determined by a flotation and a determination of the density of the floating liquid by a Westphal balance gave the value 0.509 for the ratio m/n^3 , in which m represents the number of molecules in the unit of structure and n the order of the spectrum. From an examination of a table⁴ of possible values of m/n^3 it is evident that either $m = 4$ with $n = 2$ or else that $m = 32$ with $n = 4$. Measurements upon reflection photographs of the corresponding bromide and iodide showed that they likewise have either 4 or 32 chemical molecules within the unit cell.

The Structure of $\text{NiCl}_2 \cdot 6\text{NH}_3$.—If it is assumed that n is 4, the mean value of the length of the side of the unit cube is found to be 10.09 Å. U. (or 10.09×10^{-8} cm.).

The observation (made on the Laue photographs) that only planes all of whose indices are odd reflect in the first order shows that, if 4 molecules are contained in the unit cell, this crystal must have the symmetry of one of the space groups T_h^3 , O^3 or O_h^5 . Neglecting the positions of the hydrogen atoms, which contain so few electrons that they cannot be located, all of the arrangements for this salt arising from these three space groups are identical.⁵ It will, moreover, be observed that, neglecting the

² Wyckoff, *Am. J. Sci.*, **50**, 317 (1920). Wyckoff and Posnjak, *THIS JOURNAL*, **43**, 2292 (1921); etc.

³ Wyckoff, *THIS JOURNAL*, **42**, 1100 (1920).

⁴ Wyckoff, *Am. J. Sci.*, **1**, 138 (1920).

⁵ All the space-group arguments of this paper are based upon a series of tables which form part of a book entitled "An Analytical Expression of the Theory of Space Groups" which is shortly to be published by the Carnegie Institution of Washington.

hydrogen atoms in both cases, the problem of the positions of the atoms in ammonium chloroplatinate already discussed in a previous article⁶ (if it be considered that chlorine atoms replace nitrogen atoms, nickel atoms replace the platinum atoms, and the nitrogen atoms of ammonia replace the chlorine atoms) is identical with the present one. In the first order region some planes with greater spacing are much more intense than those with lesser (see Table I), and hence the arrangement of the nitrogen atoms about the nickel atoms must be the same as the grouping of the chlorine atoms about the platinum atoms of ammonium chloroplatinate. The two salts are thus (except for the positions of the hydrogen atoms) completely isomorphous, and a detailed treatment of the present case is unnecessary.

An approximate determination of the position of the nitrogen atoms within the unit cell can be obtained from a study of the relative intensities of reflections from planes appearing in the first order. The calculated wave lengths and estimated intensities of relevant reflections obtained in Laue photographs are given in Table I. The customary intensity equations (strictly analogous to those prevailing in the case of ammonium chloroplatinate) have the following form for first order reflections from planes having all odd indices.

$$A = 4\bar{N}_i + 8\bar{N} (\cos 2\pi hu + \cos 2\pi kv + \cos 2\pi lu)$$

By plotting the amplitudes (or intensities) calculated by this expression for each of the planes of Table I over a range of values of u and comparing the calculated and observed relative intensities of planes having approximately the same spacings, the value of u can be located within fairly narrow limits. The presence of a strong fourth order and the absence of a third order reflection from the (111) face show that u is either near 0.25 or 0.50. The region around 0.50 can be eliminated from a consideration of first order reflections. The data recorded in Table I show that u must have a value less than 0.25 and lying probably between the limits 0.227 and 0.245. This lower limit is set by the observation that the plane $11\bar{5}3$ reflects less strongly than the more complicated plane $9\bar{7}7$. If the scattering powers of nitrogen and nickel were proportional to their atomic numbers (which probably is only very roughly true) the appearance of such planes as those of the forms 377 and $11\bar{7}7$ would locate the lower limit in the neighborhood of 0.24. The absence of marked discrepancies amongst the second order reflections from planes having even indices is in agreement with this value for u .

The coördinate positions of the atoms of $\text{NiCl}_2 \cdot 6\text{NH}_3$ within the unit cube are thus as follows:⁶ Nickel, arrangement 4(b); Chlorine, arrangement 8(c); Nitrogen, arrangement 24(a).

The placing of the hydrogen atoms presents some ambiguity. Since

⁶ Wyckoff and Posnjak, Ref. 2.

there are not 72 equivalent positions within the unit cell of any cubic crystal, it is evident that the 3 hydrogen atoms in the ammonia group cannot be equivalent to one another. Inspection of the possible space groups shows that 48 of these atoms must be alike, and different from the other 24; that is, two of the hydrogen atoms of the ammonia in this compound are different from the third. The special cases having 48 equivalent positions in the unit are different for the space groups belonging to different classes of cubic symmetry. If the correct class for this crystal were known, it would be possible to determine therefrom the manner of arrangement of the hydrogen atoms about the nitrogen atom. It can readily be shown that, were the symmetry of this crystal holohedral, or enantiomorphically hemihedral, the two like hydrogen atoms would

TABLE I
LAUE PHOTOGRAPHIC DATA FOR $\text{NiCl}_2 \cdot 6\text{NH}_3$

Form of reflecting plane	First photograph			Second photograph ^a			
	Relative spacing	Wave length	Estimated intensity	Form of reflecting plane	Relative spacing	Wave length	Estimated intensity
351	0.169	0.480	10	133	0.229	0.465	8
335	0.152	0.425	9	135	0.169	0.464	10
155	0.140	0.390	10	355	0.130	0.315	8
137	0.130	0.479	3-	337	0.130	0.358	2
355	0.130	0.473	8+	157	0.115	0.464	7
373	0.122	0.305	0.3	357	0.109	0.453	3
751	0.115	0.409	2	139	0.105	0.338	3
557	0.100	0.458	3	177	0.100	0.408	1
195	0.096	0.446	2	159	0.096	0.277	2
195	0.096	0.455	2+	159	0.096	0.293	2
377	0.096	0.440	0.2	159	0.096	0.415	5
577	0.090	0.396	0.2	359	0.093	0.277	1
197	0.087	0.377	0.5	577	0.093	0.301	1
379	0.085	0.479	0.2	1 3 11	0.087	0.373	1
1 5 11	0.082	0.483	0.2	179	0.087	0.305	1
579	0.080	0.475	0.3	559	0.087	0.365	2
599	0.073	0.378	0.1	379	0.085	0.346	2
...	1 5 11	0.082	0.462	2+
...	3 5 11	0.080	0.479	1
...	579	0.080	0.476	2
...	779	0.075	0.480	2

^a Reflections, but of intensities too weak for satisfactory comparisons, have been observed from planes of the following forms: 199, 1 7 11, 1 3 13, 1 5 13, 3 5 13, 3 9 11, 7 7 11, 1 1 15, 5 9 11, 1 3 15, 9 9 11, 9 11 11. These recorded estimates of intensity are necessarily very inexact. Especially in the data from this second photograph no quantitative significance should be attached to intensities of unity or less.

be equally shared by neighboring nitrogen atoms; consequently an ammonia group would not exist within such a crystal. This is so contrary to what would have been expected from chemical considerations that in the absence of any satisfactory crystallographic determination of its class of

symmetry, it is more natural to assign this salt to the space-group T_h^3 with paramorphic (pyritohedral) hemihedry. The positions of the hydrogen atoms thus probably become

Hydrogen: 24 atoms at $\bar{v}00$ and the other positions of special case 24(a); 48 atoms at $0u'v'$ and the other positions⁷ of special case 48(b).

The relative positions within the unit cell of the atoms of $NiCl_2 \cdot 6NH_3$ are readily seen with the aid of Fig. 7 in the previous article on the structure of ammonium chloroplatinate by remembering that in that figure the positions of the hydrogen atoms must be omitted from consideration, that nickel atoms replace platinum atoms, and that nitrogen and chlorine atoms are interchanged.

In common with practically all crystal structure determinations, it is at present impossible to eliminate uniquely all of the more complicated structures which could be developed for $NiCl_2 \cdot 6NH_3$. The simple structure having 4 molecules within the unit cell is nevertheless in such complete accord with the experimental data that there can be no doubt of its essential correctness. It would be possible to develop an arrangement having 32 molecules within the unit which would approach so very close to the simple structure as to be indistinguishable from it by any means now available. There is no reason for considering seriously such a complicated structure, and its assumption would not relieve this determination of the arrangement of the atoms of $NiCl_2 \cdot 6NH_3$ of any of its chemical implications.

The Structure of $NiBr_2 \cdot 6NH_3$.—This salt is completely analogous in its structure to the chloride. The length of the side of the unit cell having 4 molecules within it was determined to be 10.48 Å. U. An attempt was not made to effect an accurate placing of the nitrogen atoms.

The Structure of $NiI_2 \cdot 6NH_3$.—The arrangement of the atoms in this crystal is the same as that prevailing in the chloride. When $m = 4$ the length of the side of the unit cube was found to be 11.01 Å. U.

Three Laue photographs were completely analyzed in the endeavor to accumulate sufficient data to place the nitrogen atoms with accuracy. Because of the slightly imperfect character of the crystals employed and especially because of the much greater absorption of this salt, first order reflections from only a few planes with complicated indices could be attained. Some useful data from these photographs are recorded in Table II. From the plots of the amplitude against the parameter u for these planes (which are the same as those of the chloride) it is evident that u in this case also has a value somewhat under 0.25, but greater than 0.20. If the scattering powers of different elements were proportional to their atomic numbers, then the value of u could hardly be much less than 0.24.

⁷ The values of these coordinate positions will be given in "An Analytical Representation of the Theory of Space Groups" to which reference has already been made.

A further indication of the value of u is furnished by a comparison of the intensities of reflection in the second order region of planes containing even indices. Thus the two planes 035 and 343, both of which have the same relative spacing (0.171), reflect wave lengths of 0.780 Å. U. and 0.778 Å. U. with estimated intensities of 3.1 and 3.0. In the region between 0.20 and 0.25 this practical equality of reflecting powers could only be found if u has a value not much less than 0.24.

The Significance of these Structures.—According to this determination of structure all 6 of the ammonia molecules of $\text{NiX}_2 \cdot 6\text{NH}_3$ must be alike and related in the same manner to a central nickel atom to which they approach more closely than to any other atom of the compound. It seems therefore entirely appropriate to write the formula of these compounds in the customary coördination manner, $\text{Ni}[6\text{NH}_3]\text{X}_2$.

TABLE II
LAUE PHOTOGRAPHIC DATA FOR $\text{NiI}_2 \cdot 6\text{NH}_3$

Form of reflecting plane	First photograph			Second photograph			
	Relative spacing	Wave length	Estimated intensity	Form of reflecting plane	Relative spacing	Wave length	Estimated intensity
133	0.229	0.446	2	335	0.152	0.415	2
135	0.169	0.432	5	155	0.140	0.400	8
335	0.152	0.488	1	355	0.130	0.488	5
155	0.140	0.450	3	157	0.115	0.490	1
355	0.130	0.467	5	557	0.100	0.460	1
137	0.130	0.467	1	159	0.096	0.468	0.8
157	0.115	0.440	2
557	0.100	0.384	0.1
159	0.096	0.489	0.3
1 5 11	0.082	0.485	0.1
1 7 11	0.076	0.481	0.1

These hexamminates have been shown to have identically the same arrangement of their atoms as the grouping which prevails in the chemically rather dissimilar ammonium chloroplatinate. The hexamminate chloride and potassium chlorostannate, which is isomorphous with ammonium chloroplatinate, have furthermore almost identical distances between their corresponding atoms.⁸ In potassium chlorostannate at least 4 of the chlorine atoms would be ordinarily considered to be held to the tin atom by primary valence forces; but the union between the nickel atom and the neutral ammonia molecules is a typical secondary valence bonding. From this observation that ammonia molecules are just as intimately associated with a nickel atom in $\text{NiCl}_2 \cdot 6\text{NH}_3$ as are the chlorine atoms with a tin atom in potassium chlorostannate, it is difficult to escape from the conclusion that in the crystalline state there need not be differences between the arrangements of atoms held by what chemists have been accustomed to call primary and secondary valence forces.

⁸ Dickinson, *THIS JOURNAL*, **44**, 276 (1922).

In ammonium chloroplatinate it was shown that the distance between the platinum atom and the chlorine atoms is in close accord with that demanded by the principle of close packing of atoms as stated by W. L. Bragg.⁹ The same thing is true of the distance between tin and chlorine in potassium chlorostannate. In neither of these compounds, however, are the distances between any other pairs of atoms in satisfactory agreement with this principle. In these nickel halides, furthermore, contacts between atoms having the radii given by W. L. Bragg seem impossible except between nickel and ammonia. It cannot be determined whether such a contact is established in this direction, because of the uncertainty as to whether the hydrogen atom having the arrangement of 24(a) has a value of v which is greater or less than 0.24. The distance between the nickel atom and the nitrogen atom in all three halides greatly exceeds the sum of the radii of nickel and nitrogen. It was hoped that the value of u could be sufficiently accurately determined in $\text{NiI}_2 \cdot 6\text{NH}_3$ so that the possibility of a close packing between nickel atoms and ammonia groups could be definitely decided. Though this could not be conclusively done, the existing evidence seems to favor for u nearly the same value in both the chloride and iodide; if this is true, then no close packing of atoms having the radii assigned by W. L. Bragg would be possible within these crystals.

Summary

It has been shown that in the arrangement of their atoms the hexammoniates of nickel chloride, bromide, and iodide are strictly isomorphous with ammonium chloroplatinate. The dimensions of the unit cells for each of these salts and the values of the variable parameters defining the positions of the nitrogen atoms in the chloride and iodide have been estimated. The chemical significance of this structure within which some of the atoms are bound together by a purely secondary valence is mentioned.

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⁹ W. L. Bragg, *Phil. Mag.*, [6] **40**, 169 (1920).