148. *Isomorphous Replacement in Hydrated Salts. Part II. The System* $NaCl–CdCl_2–H_2O$ *and the Formation of Solid Solutions in the Systems* $NaCl–CdCl_2–NiCl_2–H_2O$ *and* $NaCl–CdCl_2–CoCl_2–H_2O$.

By Henry Bassett, Joseph H. Henshall, and George A. Sergeant.

One of the solid phases occurring in the system $CdCl_2–NiCl_2–H_2O$ is a series of solid solutions which may be written $(Cd,Ni)Cl_2,2{\cdot}5H_2O$. Large amounts of sodium chloride can enter isomorphously into these solid solutions until all the nickel and some of the cadmium have been replaced. There is a steady decrease in the water content of the solids as this replacement proceeds. The final result is the compound $2NaCl,CdCl_2,3H_2O$, which is found as a double salt in the system $NaCl–CdCl_2–H_2O$. A similar state of affairs holds in the system $CdCl_2–CoCl_2–H_2O$, but the pure sodium-free solid solutions $(Cd,Co)Cl_2,2{\cdot}5H_2O$ seem to be unobtainable.

The solid solutions have been examined chemically and in other ways, and much evidence brought forward to support the view that the compound $2NaCl,CdCl_2,3H_2O$ has the structure $[Na_2(H_2O)_2]^{\cdot\cdot}[Cd_2(H_2O)_2]^{\cdot\cdot\cdot\cdot}Cl_6$ and that solid-solution formation is due to replacement of $[Na_2(H_2O)_2]^{\cdot\cdot}$ by $[Ni(H_2O)_4]^{\cdot\cdot}$, $[Co(H_2O)_4]^{\cdot\cdot}$, or $[Cd(H_2O)_4]^{\cdot\cdot}$. The system $NaCl–CdCl_2–H_2O$ has been studied at 25°. Two double salts occur, $2NaCl,CdCl_2,3H_2O$, which has been recorded before, and $3NaCl,4CdCl_2,14H_2O$, which has not.

The numerous double salts occurring in the system $CdCl_2–NiCl_2–H_2O$ are discussed with special reference to their probable structure and their capacity to form solid solutions.

A series of solid solutions, $(Cd, Ni)Cl_2,2{\cdot}5H_2O$, crystallising in optically negative hexagons is readily obtainable, in the system $CdCl_2–NiCl_2–H_2O$, although metastable at 25°. In the corresponding cobalt system a similar series of solid solutions is only formed in presence of a small amount of sodium salt, most of which passes into the solid phase (see preceding paper, p. 647).

This surprising observation led to the discovery that the nickel series of solid solutions $(Cd,Ni)Cl_2,2{\cdot}5H_2O$ could also take up sodium chloride, and in large amounts, without the external form of the crystals, or their optical sign, being influenced. The stability of the solid solution was greatly enhanced by the introduction of sodium, just as that of the cobalt series of solid solutions had been. As the nickel solid solutions containing sodium seemed to be more stable than the corresponding cobalt preparations, and the crystals were also less fragile, they have been specially selected for detailed study. It appeared probable that a particularly striking case had been found of the process by which, in certain types of hydrated salts, the ion $[M(H_2O)_4]^{\cdot\cdot}$ can be replaced by the ion $[Na_2(H_2O)_2]^{\cdot\cdot}$ (Bassett, Bedwell, and Hutchinson, J., 1936, 1412). Further examination seems to have thoroughly confirmed this view.

Experimental.

The cobalt, nickel, and cadmium salts used in the investigations now described were prepared as noted in the preceding paper, and the sodium chloride was A.R. As it was likely that sodium was replacing nickel rather than cadmium, the system NaCl–$CdCl_2$–H_2O was first investigated, and it was found that there was a double salt $2NaCl,CdCl_2,3H_2O$ which crystallised in optically negative hexagons and which all the facts suggested should be closely related to the solid solution $(Cd,Ni)Cl_2,2{\cdot}5H_2O$.

It has now been shown that $2NaCl,CdCl_2,3H_2O$ is the end member of a continuous series of solid solutions derived from $(Cd,Ni)Cl_2,2{\cdot}5H_2O$ by replacement of all the nickel and some of the cadmium by sodium. The four-component, sodium-bearing series of solid solutions has been examined to determine the composition of various members of the series by a number of methods similar to those employed in dealing with the sodium-free series (see preceding paper). The most satisfactory, and the simplest, method was to dry the moist solid by washing with acetone, followed by air-drying at a low temperature. Attempts were also made to dry larger crystals, obtained by slow crystallisation, between filter papers, but it was not possible to remove mother-liquor completely in this way, chiefly because of the thinness and fragility of the crystals. The indicator method using mercuric chloride was also used in one experiment, but the complexity of the analysis makes this method even less reliable than when dealing with the solid solutions that contain no sodium.

TABLE I.

	$CdCl_2$, %.			$NiCl_2$, %.			NaCl, %.			H_2O, %.	
	A.	B.	C.	A.	B.	C.	A.	B.	C.	D.	E.
F (1)	—	61·67	20·04	—	15·80	7·39	1·52	—	1·58	—	21·01
F (2)	56·93	56·93	18·34	17·00	17·00	7·74	5·10	5·10	5·17	—	21·01
F (3)	57·22	57·08	18·28	15·94	15·90	7·21	6·03	6·02	6·03	21·00	—
G (4)	56·56	56·31	17·88	15·47	15·40	6·92	7·31	7·28	7·25	21·01	20·80
H (5)	57·54	56·76	17·81	14·32	14·14	6·27	7·82	7·71	7·59	21·39	—
H (6)	55·54	55·13	16·96	14·89	14·79	6·44	8·17	8·12	7·83	21·96	—
G (7)	54·08	53·72	16·22	15·05	14·95	6·38	8·77	8·71	8·24	22·52	—
F (8)	53·75	53·34	16·69	15·87	15·75	6·96	10·03	9·95	9·76	20·96	—
F (9)	54·10	54·11	17·11	12·92	12·92	5·82	13·01	13·01	12·81	19·96	—
F (10)	54·42	54·31	17·17	12·83	12·80	5·72	13·06	13·03	12·91	19·96	19·86
F (11)	53·78	53·63	17·04	10·37	10·34	4·64	17·08	17·03	16·96	19·00	18·91
F (12)	54·23	54·51	17·17	7·21	7·25	3·34	20·77	20·88	21·35	17·36	17·36
F (13)	53·38	53·31	17·39	3·90	3·89	1·80	26·71	26·67	27·39	16·13	—

TABLE II.

Indicator Method.

	Solution.		Moist solid.		Mother-liquor in moist solid, %.	Dry solid.		
	A.	B.	A.	B.		A.	B.	C.
$CdCl_2$	22·68	22·64	34·44	34·42	—	53·19	53·33	15·84
$NiCl_2$	19·74	19·71	16·93	16·92	61·58 (from A)	12·42	12·44	5·23
NaCl	2·62	2·61	6·12	6·12	—	11·73	11·74	10·94
$HgCl_2$	4·47	4·46	2·75	2·75	61·66 (from B)	—	—	—

Notes to Tables I and II.

A. Results of direct determination of metals, in wt. %.

B. Percentages of metal chlorides adjusted so that total base is equivalent to total determined chloride.

C. Molecular percentages calculated from B.

D. H_2O obtained by difference from B.

E. H_2O determined directly.

F. Solid (about 2 g.) filtered off in Buchner funnel and washed with 10 c.c. of 90% acetone, followed by 10—15 c.c. of " rectified " acetone, and finally with pure dry ether, and dried at about 25° for ½ hour. If the sodium content of the solution was low, the preliminary washing with dilute acetone could be omitted without danger of precipitating solid from the mother-liquor.

G. Solid washed first with 80% alcohol, then 90% and finally absolute alcohol, and air-dried.

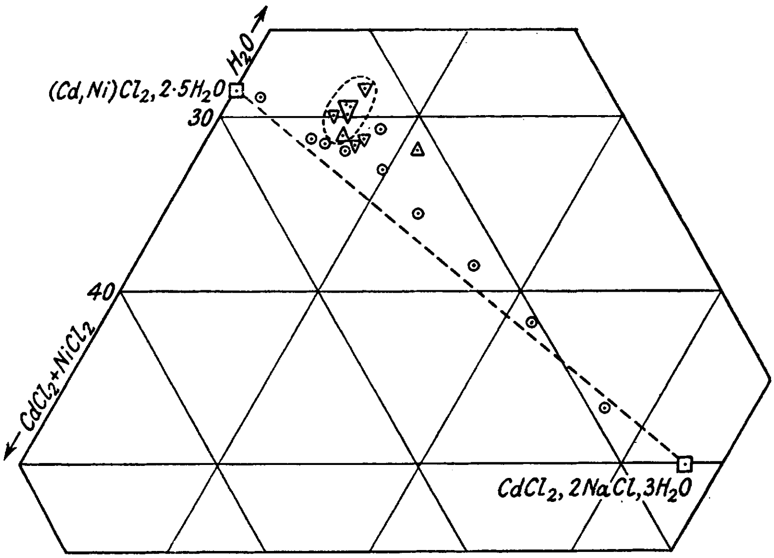
H. Larger crystals dried between filter-paper.

Analytical methods (see this vol., p. 649). Mercury, where present, was removed as metal by reduction with hydrazine and weighed as sulphide. Cadmium was removed as sulphide and weighed as $CdNH_4PO_4,H_2O$ [in (5), (6), and (7), or as $CdSO_4$ (in all other cases except (1)]. Nickel was determined electrolytically in the filtrate from cadmium sulphide, and sodium as sodium zinc uranyl acetate in a separate portion of the original solution. Mercury was removed as above before determination of chloride. Water was determined by loss of weight in ½ hour at 200°. In (1) the percentages of cadmium and nickel chlorides were calculated from estimations of total chloride, sodium, and water.

The solids were all crystallised by cooling hot saturated solutions which contained approximately equimolecular proportions of cadmium and nickel chlorides together with various proportions of sodium chloride. Except for the indicator experiment, no attempt was made to ensure isothermal equilibrium by use of the thermostat. The results appear in Tables I and II and are shown graphically in molecular percentages in Fig. 1, which shows plainly how there is a continuous transition from the pure nickel-free compound $2NaCl,CdCl_2,3H_2O$ to the sodium-free solid solution $(Cd,Ni)Cl_2,2{\cdot}5H_2O$.

In Fig. 1 the sum of the molecular percentages of cadmium chloride and nickel chloride is one co-ordinate, so the amount of each salt separately is not shown. Inspection of Table I shows that, although with increasing sodium chloride the percentages of both the foregoing salts decrease, they do so in a somewhat irregular way. This shows that, although, for a given molecular percentage of sodium chloride, the *sum* of the molecular percentages of cadmium and nickel chlorides is fixed, their *proportions* can vary to some extent. Variation of this kind has been kept within small limits by a roughly standardised method of preparation.

FIG. 1.



⊙ *Solid acetone- or alcohol-washed.*
▽ *Solid dried by filter-paper.*
△ *By indicator method.*

Points enclosed by oval dotted line refer to the corresponding cobalt system.

Had the proportions of these two chlorides used in the preparations differed more widely from equimolecular there can be little doubt that the individual ratios NaCl : $CdCl_2$ and NaCl : $NiCl_2$ would have differed somewhat from those shown in Table I. We cannot say what the extent of such variation might be. It will, of course, be limited by the fact that in the four-component system $NaCl–CdCl_2–NiCl_2–H_2O$, only solutions containing certain proportions of cadmium and nickel chlorides will be able to furnish crystals of the optically negative hexagonal solid solution. Whatever the actual proportions of the three chlorides present in the solid phase might be, it would be found that, when they are plotted in the manner of Fig. 1, a straight line in exactly the same position as in that figure would be obtained.

The optically negative hexagonal solid solution found in the system $NaCl–CdCl_2–CoCl_2–H_2O$ is in every way analogous to the nickel compound except that it is rather less stable. By slow evaporation at room temperature, hexagonal plates as large as 1 cm. in diameter have been obtained, but these were excessively thin and fragile so they could not be completely dried by means of filter-paper. Several analyses of the dried solids and the corresponding mother-liquor are shown in Table III.

One experiment was made in which sodium nitrate was added to act as an indicator substance so that, on the assumption that nitrate did not enter into the composition of the solid phase, the amount of solution in the moist solid could be determined, and hence the composition of the dry solid. The results obtained by these methods, though not very satisfactory, fell into line with the numerous results obtained with the solid solutions of the nickel series. They are shown on Fig. 1 enclosed within the oval dotted line.

These experiments with the cobalt series were carried out before those with the nickel series, and the relationship of the solid solutions to the compound $2NaCl,CdCl_2,3H_2O$ was not known then, so that a much narrower range of mixtures was examined.

TABLE III.

	G.-equiv. per 100 g. of solid (S) or liquid (L).		Weight, %.			Mols. %.		
	Cl (dir.).	Cl (ind.).	$CdCl_2$.	$CoCl_2$.	NaCl.	$CdCl_2$.	$CoCl_2$.	NaCl.
L	0·7085	0·7095	32·92	22·26	0·49	—	—	—
S	0·9492	0·9527	56·70	15·26	5·85	17·58	6·67	5·68
L	0·6828	0·6908	31·60	20·78	1·56	—	—	—
S	0·9490	0·9543	56·30	14·69	6·71	17·31	6·38	6·47
L	0·6780	0·6794	30·28	21·25	1·24	—	—	—
S	0·9475	0·9459	55·55	14·78	6·73	16·78	6·30	6·37
L	0·6863	—	33·22	19·63	1·29	—	—	—
S	0·9465	0·9455	56·32	14·47	6·36	17·11	6·20	6·05
L	0·6610	0·6648	27·46	21·82	1·82	—	—	—
S	0·9365	0·9389	54·06	14·76	7·16	15·81	6·09	6·56

Experiment with nitrate as indicator.

	G.-equiv. per 100 g. of solution (L) or filter-paper-dried solid (S).				
	Cl.	Cd.	Co.	Na.	NO_3.
L	0·6199	0·3165	0·3461	0·0261	0·0552
S	0·9265	0·5970	0·2244	0·1081	0·0060

These figures correspond to the dry solid content of $CdCl_2$, 57·92; $CoCl_2$, 13·61; NaCl, 6·92%, or 18·31, 6·07, and 6·85 mols. % respectively.

In the experiments recorded in Table III all the elements have been estimated. The figures for the three chlorides are based on determinations of the three metals; "Cl (dir.)" is the direct chloride determination, and "Cl (ind.)" gives the chlorine equivalent to the total metals found.

Cadmium was weighed as sulphate after separation as sulphide. Cobalt was weighed as Co_3O_4 after separation with α-nitroso-β-naphthol. Sodium was weighed as sodium zinc uranyl acetate. Nitrate was reduced with Devarda's alloy, and the ammonia distilled off and determined colorimetrically with Nessler's reagent. The nitrate so found was subject to an error of at least 5%.

The System $NaCl–CdCl_2–H_2O$.—A compound $2NaCl,CdCl_2,3H_2O$ was recorded by Croft (*Phil. Mag.*, 1842, **21**, 257); and Sudhaus made a phase-rule examination of this system between 19° and 55° (*Neues Jahrb. Min.*, B.-B., 1914, **37**, 1), but the conclusions were erroneous owing to the inadequacy of the analytical data.

Our work has shown that *two* double salts occur in this system, but the solubility curves when plotted on a triangular diagram might easily be mistaken for only one curve if insufficient measurements were made and if only a few moist solids were analysed. It is not easy to say just what Sudhaus did. She gives a long discussion of the various methods available for determining the formula of a double salt occurring in a three-component system, and the context rather suggests that she used the method of residues, but probably with only two tie-lines based on analyses of only two moist solids. In the paper $2NaCl,CdCl_2,3H_2O$ is accepted as the correct formula for the double salt, but no analyses of moist solids are given, or any statement that the formula has been confirmed by any of the methods discussed.

Owing to insufficient data, the second double salt was missed, although it had been expected. In addition to the invariant points, only two points on the double-salt curve are given for the 19·3° isothermal, four points on the same curve for the 29·7° isothermal, and only one each for the 40·1° and 54·5° isothermals.

Sudhaus describes $2NaCl,CdCl_2,3H_2O$ as usually occurring in wart-like masses, which she regarded as aggregates of needles. She was probably led to this erroneous conclusion by confusing the needles of $3NaCl,4CdCl_2,14H_2O$ with the supposed constituents of the aggregates.

As a matter of fact, the " wart-like " masses when disintegrated may be seen to be composed of thin irregular plates which occasionally show hexagonal outlines. In the early stages of growth or when slowly formed, the hexagonal form is often shown very clearly in crystals which are separate and not intergrown at all.

Sodium chloride, $CdCl_2,2{\cdot}5H_2O$ and $CdCl_2,H_2O$ can also occur as solid phases in this system at 25° in addition to the two above-mentioned double salts. $CdCl_2,H_2O$ is entirely metastable at this temperature.

Our results for the system $NaCl–CdCl_2–H_2O$ at 25° are shown in Table IV and Fig. 2. It should be particularly noticed that, at the cadmium chloride end of the range of the compound $2NaCl,CdCl_2,3H_2O$, and especially when it is followed into the metastable region, there is definite evidence that some replacement of sodium by cadmium is occurring. This is of considerable importance in connection with the solid solutions formed between $2NaCl,CdCl_2,3H_2O$ and $(Cd,Ni)Cl_2,2{\cdot}5H_2O$. In other words, even in the system $NaCl–CdCl_2–H_2O$, in absence of nickel (or cobalt), the compound $2NaCl,CdCl_2,3H_2O$ may be presumed to be one limit of a series of solid solutions of which the other end member would be an optically negative, hexagonal form of $CdCl_2,2{\cdot}5H_2O$. No indication has been obtained of any variability in the

TABLE IV.

System $NaCl–CdCl_2–H_2O$ *at* 25°.

	Solution.			Moist solid.			
	NaCl, %.	$CdCl_2$, % (dir.).	$CdCl_2$, % (diff.).	NaCl, %.	$CdCl_2$, % (dir.).	$CdCl_2$, % (diff.).	Solid phase.
s	26·43	nil	nil	—	—	—	a
	25·90	—	2·60	86·22	—	0·03	a
	25·50	5·25	5·53	31·39	29·32	29·56	a, b
	23·14	8·62	8·56	27·30	27·76	27·78	b
	19·95	14·42	14·65	27·40	38·62	39·04	b
	18·36	17·37	17·59	25·61	35·34	35·24	b
§	16·97	22·26	22·26	25·07	39·20	39·29	b
	15·37	27·34	27·52	21·83	36·69	36·75	b
	14·46	30·55	30·61	24·30	42·86	42·89	b
	13·78	31·76	32·31	18·32	44·13	44·76	b, c
m	12·62	37·94	37·65	17·22	42·10	41·21	b
	12·82	33·32	33·70	14·07	52·58	53·06	c
	8·65	40·75	41·06	12·13	53·30	53·69	c
	6·72	45·09	45·21	9·39	50·81	51·10	c
	4·68	50·93	50·67	7·85	54·88	54·70	c
	3·95	53·71	53·55	8·36	58·68	58·53	c, d
m	3·44	55·52	55·66	5·28	63·84	64·40	c, e
	2·61	53·55	53·50	0·56	74·96	74·92	d
	nil	54·62	—	—	—	—	d
m	2·18	55·93	56·42	1·15	72·74	72·83	e
m	nil	58·10	—	—	—	—	e

Analyses of dry solids.

	NaCl, %.	$CdCl_2$, % (dir.).	$CdCl_2$, % (diff.).	H_2O, % (dir.).	H_2O, % (diff.).	Solid phase.
*	32·42	53·02	52·63	14·95	15·35	b
	33·02	51·74	—	15·24	Calc. for b.	
†	15·02	63·90	63·64	21·34	21·43	c
	15·12	63·17	—	21·71	Calc. for c.	

Notes to Table IV.—

a. NaCl.
b. $2NaCl,CdCl_2,3H_2O$.
c. $3NaCl,4CdCl_2,14H_2O$.
d. $CdCl_2,2{\cdot}5H_2O$.
e. $CdCl_2,H_2O$.
m. Metastable.

s. From Seidell's " Solubilities of Inorganic and Organic Substances," 1911, p. 299.

* Solid was alcohol-washed and air-dried.

† Solid was acetone-washed (about 1 g. of solid washed with 5 c.c. of 90% acetone, then 5 c.c. of rectified acetone, followed by dry ether) and dried at about 25° for 20 minutes.

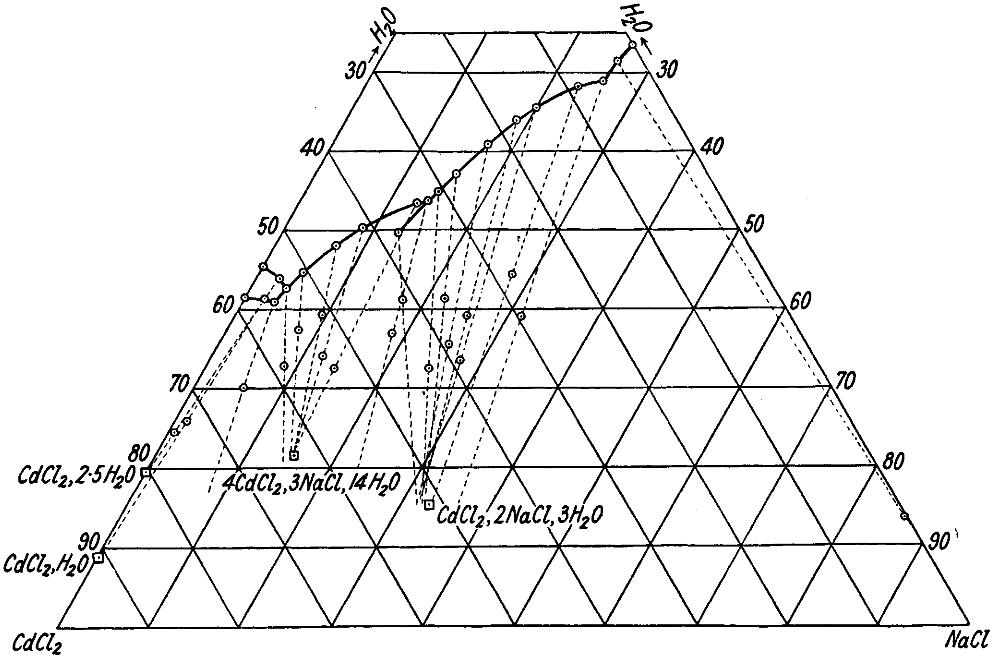
Cadmium was separated and weighed as $CdNH_4PO_4,H_2O$ in all cases except experiment marked §, in which it was separated as sulphide and weighed as sulphate; " Cd (diff.) " figures are calculated from the total chloride and sodium estimations.

Sodium was determined as sodium zinc uranyl acetate in a separate portion of solution.

composition of the other double *salt* $3NaCl,4CdCl_2,14H_2O$. The crystallising mixtures were all shaken mechanically in the 25° thermostat, usually for about 12 hours. The one mixture giving $2NaCl,CdCl_2,3H_2O$ in the metastable region was shaken by hand for 15 minutes before filtration.

We have separated for analysis dry samples of the two double salts by the acetone- or alcohol-washing method both to confirm the results given by the method of residues and to show that this method was reliable, as it was chiefly used for determining the composition of the solid solutions in the system $NaCl–CdCl_2–NiCl_2–H_2O$. As mentioned above, the compound $2NaCl,CdCl_2,3H_2O$ forms six-sided plates which are optically negative and belong to the hexagonal system. The new compound, $3NaCl,4CdCl_2,14H_2O$, forms short, flattened, pointed needles which generally show longitudinal striation and are elongated in the slow direction. The crystals are biaxial and negative and belong to the orthorhombic system, the *b* and *c* axes coinciding with the optic normal and obtuse bisectrix respectively.

FIG. 2.

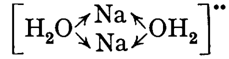


Reason for the Replacement of Nickel and Cadmium by Sodium in the Solid Solutions.—Fig. 1 shows that as the bivalent metals are replaced by sodium there is a large fall in the water content of the solid solution. It is evident, therefore, that the replacement is not simply that of $Cd^{\cdot\cdot}$ or $Ni^{\cdot\cdot}$ by $2Na^{\cdot}$. All the experimental observations are, in fact, consistent with the theory of replacement mentioned on p. **653**. According to this theory, the compound $2NaCl,CdCl_2,3H_2O$ contains both metals in the kationic condition and can be written in the form $[Na_2(H_2O)_2]_2[Cd_2(H_2O)_2]Cl_8$ or, perhaps, $[Na_2(H_2O)_2][CdH_2O]Cl_4$, although we consider that the former structure is the more likely.

Owing to sufficient similarity of form and volume the $[Na_2(H_2O)_2]^{\cdot\cdot}$ ion is replaceable by $[M(H_2O)_4]^{\cdot\cdot}$, where M may be $Cd^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, etc., and it is in this way that the solid solutions $[Cd,Ni]Cl_2,2{\cdot}5H_2O$ and $[Cd,Co]Cl_2,2{\cdot}5H_2O$ originate, although the latter appears to be too unstable to exist unless a small amount of the $[Na_2(H_2O)_2]^{\cdot\cdot}$ ion is present. These solid solutions are thus to be regarded as $[(Cd,Ni)(H_2O)_4]_2[Cd_2(H_2O)_2]Cl_8$, where (Cd,Ni) indicates that these two metals are replacing one another isomorphously. Complete replacement of $[Na_2(H_2O)_2]^{\cdot\cdot}$ by $[Ni(H_2O)_4]^{\cdot\cdot}$ would lead to the simple compound $[Ni(H_2O)_4]_2[Cd_2(H_2O)_2]Cl_8$ or $CdCl_2,NiCl_2,5H_2O$, which has not been obtained because replacement of $[Na_2(H_2O)_2]$ by both $[Cd(H_2O)_4]$ and $[Ni(H_2O)_4]$ occurs simultaneously.

This is due, presumably, to a relatively high concentration of $[Cd(H_2O)_4]^{\cdot\cdot}$ ions in spite of the fact that when solid cadmium chloride separates at 25° it does so as $CdCl_2,2{\cdot}5H_2O$ or $CdCl_2,H_2O$. The hydrate $CdCl_2,4H_2O$, *i.e.*, $[Cd(H_2O)_4]Cl_2$, is only stable below − 5° in the system $CdCl_2$–H_2O, although it will separate as a metastable form up to at least + 15° (Seidell, *op. cit.*, p. 73).

Since nickel tends to be much more hydrated in its compounds than cadmium, it is unlikely that under the conditions where $(Cd,Ni)Cl_2,2{\cdot}5H_2O$ separates any of the nickel is in the $[Cd_2(H_2O)_2]^{\cdot\cdot\cdot\cdot}$ constituent.

X-Ray powder photographs have been taken of the compound $2NaCl,CdCl_2,3H_2O$ and of several of the solid solutions spaced over the range from the pure sodium compound to the sodium-free $(Cd,Ni)Cl_2,2{\cdot}5H_2O$. The majority of the lines of the pure sodium compound occur in all the photographs, but certain lines get fainter and fainter with decreasing contents of NaCl and new lines appear, not very far away, and these get stronger as $(Cd,Ni)Cl_2,2{\cdot}5H_2O$ is approached. All the preparations used for the examination consisted of moderately large crystals which, according to ordinary crystallographic standards, appeared to be perfectly clear and homogeneous. The *X*-ray evidence in no way suggests that ordinary mixtures are involved, nor is it opposed to the views put forward as to the structure and origin of these curious solid solutions. We are commencing a complete *X*-ray structural examination of $2NaCl,CdCl_2,3H_2O$ and its derived solid solutions. If the planar  $\left[H_2O\begin{smallmatrix}\nearrow Na \searrow\\ \searrow Na \nearrow\end{smallmatrix}OH_2\right]^{\cdot\cdot}$ can be replaced by $[Ni(H_2O)_4]^{\cdot\cdot}$, the latter must presumably be planar also. According to Pauling's arguments (*J. Amer. Chem. Soc.*, **1931**, **53**, 1367) planar quadricovalent nickel should be diamagnetic, but a sample of the solid solution material was found to be paramagnetic to the degree calculated from the known value for paramagnetic nickel. There are reasons for considering that planar $[Ni(H_2O)_4]^{\cdot\cdot}$ may be present in spite of this result. The tendency to form large, excessively thin, plates, which is a characteristic feature of the solid solutions $[Cd,Ni]Cl_2,2{\cdot}5H_2O$, is in excellent agreement with the view that all the constituent kations are planar (for $[Cd_2(H_2O)_2]^{\cdot\cdot\cdot\cdot}$ would be planar just like $[Na_2(H_2O)_2]^{\cdot\cdot}$). $CdCl_2,2NiCl_2,12H_2O$ is also hexagonal but does not seem to have nearly as good a cleavage parallel to the base of the hexagonal prism, and this may be because all the kations are not planar (see the constitution suggested for it on p. **660**).

Although our evidence for structures is still very incomplete, we consider that it is sufficient to justify the following discussion of the nature of the double salts shown by us to exist in the systems $CdCl_2$–$NiCl_2$–H_2O and $CdCl_2$–$CoCl_2$–H_2O.

In the system NaCl–$CdCl_2$–H_2O it has been shown that the compound $2NaCl,CdCl_2,3H_2O$ can contain more cadmium than corresponds to this formula. This is because of replacement of $[Na_2(H_2O)_2]^{\cdot\cdot}$ by $[Cd(H_2O)_4]^{\cdot\cdot}$ as the concentration of sodium relative to cadmium falls off. No replacement of $[Cd_2(H_2O)_2]^{\cdot\cdot\cdot\cdot}$ by sodium is possible, so at the sodium end of the series the composition of the compound is fixed.

Complete replacement of $[Na_2(H_2O)_2]^{\cdot\cdot}$ by $[Cd(H_2O)_4]^{\cdot\cdot}$ never occurs, either because some entirely different solid phase becomes the stable solid, *e.g.*, $3NaCl,4CdCl_2,14H_2O$, or else because the requisite concentrations of the two ions $[Cd(H_2O)_4]^{\cdot\cdot}$ and $[Cd_2(H_2O)_2]^{\cdot\cdot\cdot\cdot}$ are never reached. Since the pure, optically negative, hexagonal $[Cd(H_2O)_4]_2[Cd_2(H_2O)_2]Cl_8$ has never been recorded, one may conclude that for some reason an alternative structure is more stable, such as $[Cd(H_2O)_4][Cd(H_2O)_2]_3Cl_8$, which may correspond to the well-known $CdCl_2,2{\cdot}5H_2O$. This is only one of several possibilities, and since there is not the same disparity in the degree of hydration of the two kinds of cadmium kations as in the other structure, it seems more likely to be stable. The case is altered, however, as soon as one is dealing with solutions containing both cadmium and nickel ions with very different hydration tendencies, so that $[(Cd,Ni)(H_2O)_4]_2[Cd_2(H_2O)_2]Cl_8$ becomes a relatively stable structure, since a deficiency of $[Cd(H_2O)_4]^{\cdot\cdot}$ in the nickel-free solutions is compensated for by plenty of $[Ni(H_2O)_4]^{\cdot\cdot}$ in the mixed solutions.

It is to be noted that if the ordinary $CdCl_2,2{\cdot}5H_2O$ does have the structure $[Cd(H_2O)_4][Cd(H_2O)_2]_3Cl_8$ some replacement of $[Cd(H_2O)_4]^{\cdot\cdot}$ by $[Na_2(H_2O)_2]^{\cdot\cdot}$ should be possible. The range of existence of $CdCl_2,2{\cdot}5H_2O$ in the system NaCl–$CdCl_2$–H_2O is so small, however, that one cannot expect such replacement to be detectable. The alternative structure $[(H_2O)_2Cd(H_2O)_2Cd(H_2O)_2][Cd(H_2O)_2]_2Cl_8$ would not permit of any replacement by sodium.

It is noteworthy that, of the numerous double salts in the system $CdCl_2$–$NiCl_2$–H_2O, only $(Cd,Ni)Cl_2,2{\cdot}5H_2O$ and $CdCl_2,2NiCl_2,12H_2O$ appear to belong to series of solid solutions. There must be some reason for this, and we attribute it to the large difference in the degree of hydration of the constituent nickel and cadmium kations in most of the double salts. This results in the ions which would be needed if solid solutions were to be formed being present in insufficient concentration in the liquid solutions to enter into the solid phase. Only in the few instances where the corresponding ions of the two metals are present in comparable amounts can solid solutions be formed.

A structure $[Cd(H_2O)_2][Ni(H_2O)_4][Ni(H_2O)_6]Cl_6$ would account for all the facts observed with the double salt $CdCl_2,2NiCl_2,12H_2O$. At the nickel end of the system, the presence of $[Ni(H_2O)_4]^{\cdot\cdot}$ and $[Ni(H_2O)_6]^{\cdot\cdot}$, both in large amount, is reasonable and likely, but it is not likely that there is any appreciable amount of $[Ni(H_2O)_2]^{\cdot\cdot}$. Hence at this end of the region, over which this double salt can separate at 25°, it behaves as a definite compound, but as one goes over towards the cadmium side the proportion of $[Cd(H_2O)_4]^{\cdot\cdot}$ ions in solution relative to $[Ni(H_2O)_4]^{\cdot\cdot}$ increases so that some replacement occurs in the solid phase. It is unlikely that sufficient $[Cd(H_2O)_6]^{\cdot\cdot}$ is present in the solution for any replacement of $[Ni(H_2O)_6]^{\cdot\cdot}$ by this ion to occur. Should this replacement of $[Ni(H_2O)_4]$ by $[Cd(H_2O)_4]$ be able to go to completion under any circumstances it would yield a hexagonal form of $2CdCl_2,NiCl_2,12H_2O$ as the other end member of this series of solid solutions.

Experience in the system $CdSO_4$–$CoSO_4$–H_2O (Bassett and Sanderson, J., **1934**, **1116**) makes it practically certain that any hydrated cadmium kation which may be present in any of the double chlorides under discussion could be replaced isomorphously by the corresponding nickel or cobalt kation if present in sufficient concentration. All the double salts which occur must therefore be regarded as end members of possible series of solid solutions which might be formed at some other temperature or in some other circumstances.

Since $2CdCl_2,NiCl_2,12H_2O$ is not isomorphous with $CdCl_2,2NiCl_2,12H_2O$ and does not form solid solutions over the region in which it occurs, it cannot very well have the same constitution. The structure $[(H_2O)_2Cd(H_2O)_2Cd(H_2O)_2][Ni(H_2O)_6]Cl_6$ for this compound seems not unlikely, and would explain the facts as at present known. The lower hydrate $2CdCl_2,NiCl_2,6H_2O$ would then be $[Cd(H_2O)_2Cd][Ni(H_2O)_4]Cl_6$ in all probability. Obvious possibilities for the remaining double salts are $[Cd(H_2O)_2]_3[Ni(H_2O)_4]_2Cl_{10}$ for $3CdCl_2,2NiCl_2,14H_2O$, and $[Cd(H_2O)_2Cd]_2[Ni(H_2O)_6]Cl_{10}$ for $4CdCl_2,NiCl_2,10H_2O$. In both these cases it is unlikely that corresponding ions of the second metal would be present in sufficient concentration to produce any measurable solid solution effect.

Finally, it may be pointed out that, since cadmium, nickel, and cobalt can all be replaced by sodium in these double salts, one is fully justified in assuming that these metals are present entirely in the kationic condition.

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