253. *The Compounds of Lithium Chloride with Cobalt Chloride. Water as a Linking Agent in Polynuclear Kations.*

By Henry Bassett and Isabella Sanderson.

An endeavour is being made in these laboratories to elucidate the nature of compounds of the common metals in which the latter appear to have low and unusual co-ordination numbers, the term co-ordination being used in the sense in which Werner used it and not in its crystallographic sense (Bassett and Croucher, J., 1930, 1786). Sidgwick's rule (J., 1924, **125**, 532) gives us the maximum values of the co-ordination numbers of the various elements, but at present we have very scanty information as to what lower stages are normally possible.

As with many other questions concerning co-ordination, the problem has to be dealt with to some extent statistically, and for that reason will entail much work in re-examining the evidence for many of the compounds given in the literature. So many of these do not exist at all and so many have been given erroneous formulæ, particularly as regards the degree of hydration, that false deductions are easily drawn when the material is employed statistically.

The whole question of co-ordination numbers is linked up with that of complex-ion formation, and we have found the study of cobaltous salts particularly useful for our purpose owing to the fact that kationic cobalt seems to be always red and anionic almost always blue, while in the non-ionic condition it generally gives rise to a pale blue colour distinct from that of the anionic blue.

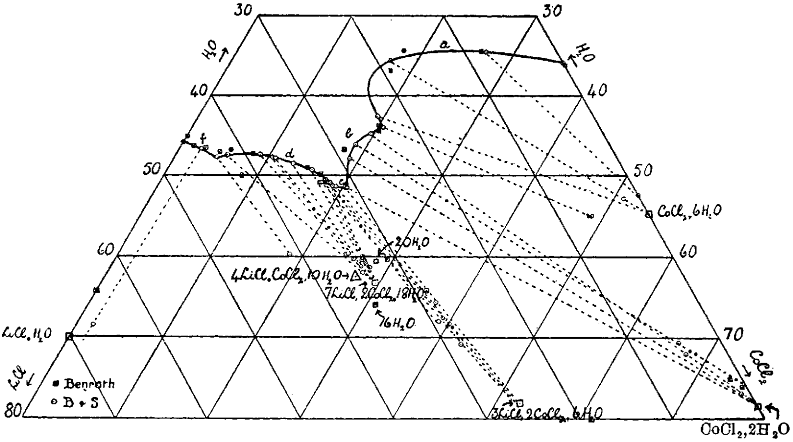
We were particularly anxious to obtain further information in respect of the less symmetrical complex anions such as $[CoCl_3,H_2O]'$ in connexion with work on cobalt chloride solutions (Bassett and Croucher, *loc. cit.*). For these reasons we have studied the system $CoCl_2$–LiCl–H_2O at several temperatures.

Chassevent (*Ann. Chim. Phys.*, 1893, **30**, 5) stated that he had obtained the compound $LiCl,CoCl_2,3H_2O$, of which he gave good analyses. He described it as forming fine sapphire-blue prisms which could be recrystallised unchanged from alcohol, and said it was formed when concentrated solutions of cobalt and lithium chlorides were mixed at ordinary temperatures. Unfortunately, he gives no details of the concentrations, quantities, or temperatures actually employed by him, so it is difficult to repeat his work.

As will be seen later, we have failed to obtain this compound, though we have obtained several others. It is possible that, by some chance, Chassevent may have obtained $LiCl,CoCl_2,3H_2O$. The compound $HCl,CuCl_2,3H_2O$ appears to be definitely established by Foote's phase-rule investigation (*J. Amer. Chem. Soc.*, 1923, **45**, 663) and its existence might be regarded as rendering that of the above-mentioned complex chloride likely, in spite of the fact that no solid $HCl,CoCl_2,3H_2O$ could be isolated (Bassett and Croucher, *loc. cit.*). We should expect it to be capable of existence if solubility conditions would allow it to separate, but we have come to the conclusion that they do not. The fact that at 60° there is only a very short range of solutions in stable equilibrium with $LiCl,CoCl_2,2H_2O$ between the curves for $CoCl_2,2H_2O$ and $3LiCl_2,CoCl_2,6H_2O$, shows that the latter intersect in the stable region at a slightly lower temperature, so that there is no room for a compound $LiCl,CoCl_2,3H_2O$ except, possibly, as a metastable phase. Chassevent's description of the colour of his compound agrees well with that of our $LiCl,CoCl_2,2H_2O$, and it is possible that the solid analysed by him consisted of this in a somewhat moist condition. $7LiCl,2CoCl_2,18H_2O$ is the only one of the complex salts isolated which we should describe as forming fine *prisms*. If this is the compound obtained by Chassevent, it is much more difficult to account for his analyses. All these solids are extremely difficult to obtain dry and our attempts to use alcohol for purification hardly support Chassevent's statement.

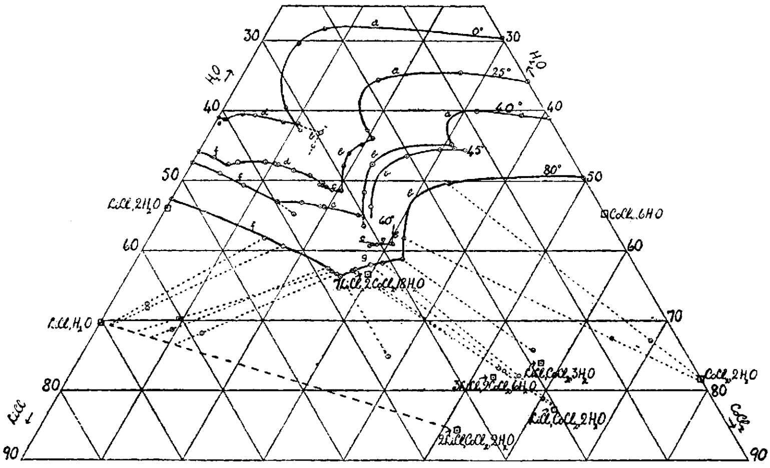
Benrath (*Z. anorg. Chem.*, 1927, **163**, 396) examined the system at 25° and stated that a compound $4LiCl,CoCl_2,10H_2O$ was formed. His conclusion is quite erroneous, however, and this is chiefly owing to a fault from which much of his work seems to suffer, namely, lack of sufficient observations. His solution points do not fall very well on our curves, but the few tie-lines that can be drawn from his scanty results in the double-salt region agree much better with our results than with his conclusions. His points are shown on Fig. 1.

FIG. 1.



In the anhydrous system, LiCl–$CoCl_2$, one compound, 2LiCl,$CoCl_2$, was indicated by the results of Ferrari (*Atti R. Accad. Lincei*, 1928, 7, 848). We have studied the system LiCl–$CoCl_2$–H_2O at 0°, 25°, 40°, and 80°, a few observations being also made at 45° and 60°. The results of our measurements are summarised in the tables, and represented graphically in Figs. 1 and 2.

FIG. 2.



The isotherm for 0° shows portions corresponding to the compounds $CoCl_2,6H_2O$; $CoCl_2,2H_2O$; $LiCl,2H_2O$, and the double *salt* $7LiCl,2CoCl_2,18H_2O$; but $CoCl_2,2H_2O$ is entirely a metastable phase at 0°. At 25° the solid phases are $CoCl_2,6H_2O$; $CoCl_2,2H_2O$; $LiCl,H_2O$, and two double salts, the one found at 0°

$$(7LiCl,2CoCl_2,18H_2O)$$

and a new *compound* richer in cobalt chloride ($3LiCl,2CoCl_2,6H_2O$). At 40° the solid phases are the same as at 25° except that the compound $7LiCl,2CoCl_2,18H_2O$ has disappeared. At 80° the isotherm consists of only three branches, one corresponding to $CoCl_2,2H_2O$, one to a new double *salt* $LiCl,CoCl_2,2H_2O$, and the third appears, at first sight, to correspond to $LiCl,H_2O$.

It is found, however, that the tie-lines corresponding to this branch of the isotherm show, in an exaggerated degree, what was already noticeable in the corresponding branches of the isotherms for 40° and for 25°. The tie-lines do not all run to the point corresponding to the compound $LiCl,H_2O$, but they spread out in the manner which always indicates that the solid phase consists of a series of solid solutions. It is certain that these are based upon $LiCl,H_2O$, for the well-formed crystals have the regular octahedral form characteristic of this hydrate. The nature of the other constituent of the solid solution is clearly a matter of some interest, but before discussing this problem it is advisable to consider the probable nature of the several double salts found in the system.

Since these all possess a fine blue colour, it can be accepted (Bassett and Croucher, *loc. cit.*) that they all contain the whole of the cobalt in the anionic condition.

$LiCl,2H_2O$ is presumably $[Li(H_2O)_2]^{\cdot}Cl'$, in which the lithium atom has a co-ordination number 2. According to Sidgwick's rule, the maximum co-ordination number of lithium is 4, and all the lithium atoms in the compound $7LiCl,2CoCl_2,18H_2O$ seem to be 4-co-ordinated. The only reasonable way of formulating the compound appears to us to be as follows :

$$[Li_4(H_2O)_{10}]^{IV}[Li_3(H_2O)_8]^{III}[Cl_5Co{-}Cl{-}CoCl_5]^{VII}$$

This shows a polynuclear anion containing two 6-co-ordinate cobalt atoms linked through one chlorine atom, the anion carrying seven negative charges. These are balanced by two polynuclear kations of the chain type (Bassett and Croucher, *loc. cit.*, p. 1803).

One of these contains four lithium atoms and the other three, all linked through two water molecules thus

$$[(H_2O)_2Li(H_2O)_2Li(H_2O)_2Li(H_2O)_2Li(H_2O)_2]^{\cdot\cdot\cdot\cdot}$$

and $[(H_2O)_2Li(H_2O)_2Li(H_2O)_2Li(H_2O)_2]^{\cdot\cdot\cdot}$. It appears to us probable that this very complex compound may really have resulted from the linking together of the two anions $[CoCl_6]''''$ and $\left[\begin{matrix}CoCl_5\\H_2O\end{matrix}\right]'''$ corresponding to the above two kations with elimination of the molecule of water. These two relatively simple anions are probably both present in the blue solutions, though it would seem that solubility relationships are such that no solid compound actually containing them is able to separate from the lithium chloride system. It is conceivable that the complex double anion does not actually exist as such in the solution, but is only built up during crystal formation. Had the compound only contained 16 molecules of water instead of 18, it would have been possible to formulate it with a single polynuclear kation of the same type as the two we have actually assumed. The position of the point for the $16H_2O$ compound on the diagram shows that our compound must have contained $18H_2O$.

The compound $3LiCl,2CoCl_2,6H_2O$ appears to show a precisely similar process occurring with two anions containing 4-co-ordinated cobalt, and we formulate it as $[Li(H_2O)_2]^{\cdot}_3\ [Cl_3CoClCoCl_3]'''$, the anion in this case resulting from the linking of $[CoCl_4]''$ and $\left[Co^{Cl_3}_{H_2O}\right]'$.

The salt $[Li(H_2O)_2]^{\cdot}\left[\begin{matrix}CoCl_3\\H_2O\end{matrix}\right]'$ corresponding to the last ion would be Chassevent's compound, while the anion $[CoCl_4]''$ corresponds to the anhydrous $Li^{\cdot\cdot}_2[CoCl_4]''$ found by Ferrari (*loc. cit.*). Our last compound $LiCl,CoCl_2,2H_2O$ may also be a salt derived from the $\left[Co^{Cl_3}_{H_2O}\right]'$ ion, *i.e.*, $[Li(H_2O)]^{\cdot}\left[Co^{Cl_3}_{H_2O}\right]'$, but we feel uncertain about this for reasons now to be discussed in connexion with the solid solutions based on $LiCl,H_2O$. The positions of the tie-lines relating to the latter suggest very strongly that the second constituent of the series of solid solutions is the compound $2LiCl,CoCl_2,2H_2O$. When the latter is given the structure $[Li_2(H_2O)_2]^{\cdot\cdot}[CoCl_4]''$, and lithium chloride monohydrate one corresponding to a termolecular formula $[Li_2(H_2O)_2]^{\cdot\cdot}\left[Li^{Cl_3}_{H_2O}\right]''$, the formation of such solid solutions is seen to be quite reasonable, especially when calculation shows that the molecular volumes of $\left[Li^{Cl_3}_{H_2O}\right]$ and $[CoCl_4]$ are very nearly the same (94 and 92·4 respectively). This evidence that lithium chloride monohydrate is really $(LiCl,H_2O)_3$ was unexpected and immediately raises the question as to the cause of the polymerisation. Had the monohydrate really had the unimolecular formula, it would have been $[Li(H_2O)]^{\cdot}Cl'$ in which the lithium would have had a co-ordination number 1. It is highly probable that such an unsymmetrical

1-co-ordinated lithium ion would be unstable with respect to the 2- or 4-co-ordinated condition. The simple chlorine ion is a perfectly stable structure though very ready to act as an electron " donor " and become co-ordinated to other atoms which are short of electrons. The chlorine cannot be held responsible for the polymerisation of the monohydrate, though it helps to make it possible. The real cause of the polymerisation is to be sought in the need for the lithium to become either 2- or 4-co-ordinated. This it does by co-ordination, partly with chlorine ions and partly with water, to give the structure $\left[\mathrm{Li}{}^{\mathrm{H_2O}}_{\mathrm{H_2O}}\mathrm{Li}\right]^{\cdot\cdot}\left[\mathrm{Li}{}^{\mathrm{Cl_3}}_{\mathrm{H_2O}}\right]''$. It is the oxygen atoms of the water molecules which are co-ordinated to the lithium, both in the kation and in the anion. The water available in the solutions from which this compound separates and the spatial requirements of the crystals do not permit of each lithium atom having two water molecules to itself, so the two lithium atoms have to share the two water molecules, one bivalent binuclear kation being produced instead of two univalent kations. The above argument appears to make it quite clear that in this compound there is really a complex kation of the kind indicated. We consider that the compound affords direct proof of the correctness of the view (Bassett and Croucher, *loc. cit.*, p. 1803) that in polynuclear kations linkage through water molecules can and frequently does occur.

This instability of 1-co-ordinated lithium makes it unlikely that our compound $\mathrm{LiCl,CoCl_2,2H_2O}$ has the structure $[\mathrm{LiH_2O}]^{\cdot}\left[\mathrm{Co}{}^{\mathrm{Cl_3}}_{\mathrm{H_2O}}\right]'$. It is much more likely that it is $[\mathrm{Li(H_2O)_2Li}]^{\cdot\cdot}\left[\mathrm{Co}{}^{\mathrm{Cl_3}}_{\mathrm{H_2O}}\right]'_2$, although the possibility cannot be entirely excluded that it is

$$[\mathrm{Li(H_2O)_2}]^{\cdot}_2[\mathrm{Cl_2CoCl_2CoCl_2}]''.$$

It is of interest to compare the compounds of rubidium and cæsium chlorides with cobalt chloride with those formed by lithium chloride. The rubidium and cæsium compounds have been examined by Foote at 25° (*Amer. J. Sci.*, 1927, **13**, 158), and the compounds found agree very well with both our experimental results for the lithium compounds and the deductions we have drawn from them.

The rubidium compounds found were $\mathrm{2RbCl,CoCl_2,2H_2O}$ and $\mathrm{RbCl,CoCl_2,2H_2O}$, and those of cæsium were $\mathrm{3CsCl,CoCl_2}$, $\mathrm{2CsCl,CoCl_2}$, and $\mathrm{CsCl,CoCl_2,2H_2O}$. The two compounds of type $\mathrm{RCl,CoCl_2,2H_2O}$ clearly correspond to our lithium compound of the same type and will, presumably, have a similar structure, while $\mathrm{2RbCl,CoCl_2,2H_2O}$ corresponds to the $\mathrm{2LiCl,CoCl_2,2H_2O}$ constituent of our solid solutions, to which it gives important support.

$\mathrm{2RbCl,CoCl_2,2H_2O}$ and $\mathrm{2CsCl,CoCl_2}$ are derived from the $\mathrm{CoCl_4}''$

ion, the anhydrous cæsium compound Cs_2CoCl_4 corresponding to Ferrari's anhydrous lithium compound. Whether in the case of the hydrated rubidium compound one has the binuclear kation $[Rb(H_2O)_2Rb]^{\cdot\cdot}$ or two $[RbH_2O]^{\cdot}$ kations, it is not easy to say. In all probability all alkali-metal compounds which appear to contain $[M,H_2O]^{\cdot}$ ions really contain the binuclear $[M,(H_2O)_2M]^{\cdot\cdot}$ ion. We should formulate the anhydrous $3CsCl,CoCl_2$ as $Cs'_6[Cl_4CoCl_2CoCl_4]^{VI}$ with a binuclear complex anion containing two 6-co-ordinated cobalt atoms. It is well known that cæsium compounds have an even greater tendency to be anhydrous than have rubidium compounds. It is probable that a completely anhydrous alkali-metal ion is, in many ways, more stable than a monohydrated one would be, though not necessarily more so than a dihydrated one.

Neither sodium nor potassium chloride forms any compounds with cobalt chloride at 25° (Foote, *loc. cit.*; Benrath, *loc. cit.*) or at 20° (Mazzetti, *Gazzetta*, 1926, **56**, 601). They both tend to turn cobalt chloride solutions blue, as do the chlorides of the other alkali metals, but solubility relationships are unsuitable for the separation of solid complex salts from aqueous solution.

Benrath (*loc. cit.*) also examined the systems $RbCl–CoCl_2–H_2O$ and $CsCl–CoCl_2–H_2O$ at 25°. In the latter he found the same compounds as Foote, but he could not find the rubidium compound $RbCl,CoCl_2,2H_2O$ and thought that it was a mixture of $CoCl_2,6H_2O$ and $2RbCl,CoCl_2,2H_2O$. We consider, however, that more value must be given to Foote's results than to Benrath's.

EXPERIMENTAL.

The materials employed were iron- and nickel-free cobalt chloride hexahydrate and anhydrous lithium chloride. The purity of the latter was considered satisfactory from the results obtained in the determination of the solubility of lithium chloride in pure water at 25° (solid phase $LiCl,H_2O$). Evaporation of the solution and conversion to sulphate gave a content of 45·98% LiCl in the saturated solution, whereas a determination of the chloride as silver chloride gave a value of 45·85% LiCl. This value for the solubility agrees very well indeed with Friend's most recent determinations (J., 1931, 3148) and so do our values for 0°, 40°, and 80°.

Mixtures for each individual experiment were prepared from suitable weighed amounts of the two chlorides and water to give about 10 g. of solution and 1—2 g. of solid phase. All the solid was dissolved by heating, and the mixtures were allowed to crystallise at the experimental temperature. The mixtures were contained in thin, hard-glass bottles closed by corks. The latter were waxed at 0° and 25° but not at the higher temperatures. At 40° and above, the bottles were hung in the thermostat with the corks projecting and were shaken frequently by hand. We found that attainment of equilibrium between solid and solution was rapid at all temperatures.

The contents of the bottles were filtered in a jacketed filter tube. The moist solid was well pressed while in the tube on the pump, and then between filter paper. Cobalt and total chloride were estimated in solution and moist solid, the former as Co_3O_4 after precipitation with α-nitroso-β-naphthol and strong ignition, the latter gravimetrically. These results enabled the percentages of cobalt and lithium chlorides to be calculated.

Temperature = 0°.

Solution.		Moist solid.		Solid phase.*	Solution.		Moist solid.		Solid phase.*
$CoCl_2$.	LiCl.	$CoCl_2$.	LiCl.		$CoCl_2$.	LiCl.	$CoCl_2$.	LiCl.	
29·50	—	—	—	a	10·47	31·56	38·13	14·69	a & d
6·92	21·30	46·62	3·61		8·45	33·21	25·01	33·08	d
4·75	25·67	43·75	5·42		4·41	36·24	23·17	33·82	
7·71	31·90	42·68	8·18		2·82	37·68	20·54	35·38	
†11·06	31·73	46·52	5·99		0·92	40·43	17·50	39·41	d & e
†13·87	29·48	24·85	31·83	b & d	0·85	40·53	5·96	46·91	
†13·81	31·32	54·17	12·12	b	—	40·87	—	—	e

† Metastable region.

* a = $CoCl_2,6H_2O$.
b = $CoCl_2,2H_2O$.
c = $3LiCl,2CoCl_2,6H_2O$.
d = $7LiCl,2CoCl_2,18H_2O$.
e = $LiCl_2,2H_2O$.
f = Solid solution.
g = $LiCl,CoCl_2,2H_2O$.
h = $LiCl,H_2O$.

The lettering on the curves in Figs. 1 and 2 is in accordance with that in this table.

Temperature = 25°.

35·87	—	—	—	a	18·24	32·45	38·71	29·27	d & c
26·81	7·82	52·25	—		18·36	32·68	41·20	28·76	
17·11	18·61	50·94	1·84		17·60	32·96	27·94	33·48	d
19·36	23·36	54·89	—		15·53	33·85	26·64	33·91	
20·56	23·48	48·86	6·11	a & b	13·08	35·44	25·90	34·37	
19·69	25·07	75·83	0·97	b	10·75	36·98	24·79	34·94	
18·72	27·45	66·00	4·58		‡10·65	37·14	26·93	34·22	
18·97	28·94	67·44	4·63		9·00	38·31	24·54	35·01	
20·32	31·06	77·00	0·40		‡ 5·58	41·95	27·45	34·62	
20·16	31·12	37·26	28·49	c	4·55	43·11	18·40	41·23	d & f
19·20	32·19	38·95	28·57		2·40	44·39	1·62	66·87	f
†17·25	33·24	39·97	28·31		—	45·85	—	—	h

‡ Large crystals.

Temperature = 40°.

40·96	—	—	—	a	24·30	30·68	35·96	28·94	c
37·31	3·33	50·00	0·80		19·51	34·29	33·29	30·99	
31·60	8·60	53·62	0·43		18·97	34·73	35·85	30·82	
31·35	13·94	49·61	3·35		16·36	36·75	35·94	31·09	
30·85	14·06	62·35	1·87	a & b	13·19	39·74	23·83	40·63	c & f
22·40	25·10	69·21	3·81	b	†16·04	38·66	9·13	54·34	f
23·35	28·19	67·30	5·31		7·97	42·71	3·72	62·30	
†25·71	30·76	54·77	14·41		4·17	44·88	2·65	56·95	
24·99	30·06	47·58	18·27	b & c	—	47·47	—	—	h

Temperature = 45°.

Solution.		Moist solid.			Solution.		Moist solid.		
$CoCl_2$.	LiCl.	$CoCl_2$.	LiCl.	Solid phase.*	$CoCl_2$.	LiCl.	$CoCl_2$.	LiCl.	Solid phase.*
32·93	12·78	69·56	1·65	b	26·13	20·33	65·66	4·32	b
29·76	15·84	65·60	3·75		25·52	28·56	63·11	7·93	
Temperature = 60°.									
30·23	28·80	68·31	5·79	b	28·62	30·57	47·90	26·74	c & g
30·62	28·67	54·56	21·76	b & g	†27·84	31·64	57·46	22·02	g
Temperature = 80°.									
49·5	—	—	—	b	26·29	37·25	38·00	37·05	f & g
33·23	17·19	69·36	3·39		(i) 25·85	37·48	13·32	58·51	f
31·67	26·67	64·29	8·10		(ii) 24·99	37·93	9·28	60·46	
32·84	28·44	55·52	18·74	b & g	24·38	38·23	9·27	61·90	
30·73	31·01	55·61	22·23	g	17·16	42·09	4·86	64·56	
29·26	32·81	60·10	20·98		14·26	43·90	4·50	63·20	
27·56	35·02	53·31	23·82		—	52·71	—	—	h
27·49	35·20	52·52	24·26						

(i) 0·3 G. of solid phase in 10 g. of solution.
(ii) 3 G. of solid phase in 5 g. of solution.

The extent to which solution could be removed from the moist solids depended partly on the nature of these. The compound $3LiCl,2CoCl_2,6H_2O$ separates in very small needles, so it could never be obtained for analysis in anything but a relatively very wet condition, which accounts for the points in Fig. 1 corresponding to the moist solid being a long way from the point corresponding to the dry solid. In general, the wetness of all moist solids, as judged by eye, agreed well with the positions as plotted. This is of especial importance in connexion with the solid solutions of curve *f*, Fig. 2, and supports our method of drawing the solidus.

The exact slope of the tie-lines in the region of solid solutions was found to depend upon the amount of solid phase separating from a given solution. This is bound to be the case (Bassett and Croucher, *loc. cit.*, p. 1804). In the present instance it was found that the tie-lines were steeper the smaller the amount of solid phase separating, and this is illustrated by experiments (i) and (ii) in the last table.

All the complex salts are blue, but the colour of $LiCl,CoCl_2,2H_2O$ is quite distinctive, being sapphire-blue, *i.e.*, of a purer and less purple blue than the other compounds.

The compounds are readily distinguishable by their crystalline form. $7LiCl,2CoCl_2,18H_2O$ forms large prisms with pointed ends, the terminal angle being about 90°. The crystals are usually about twice as long as they are broad. $3LiCl,2CoCl_2,6H_2O$ forms very small needles with obliquely truncated ends. Owing to the smallness of these crystals, they appear much paler in colour than do the crystals of the other compounds. $LiCl,CoCl_2,2H_2O$ forms diamond-shaped plates, generally grouped in clusters. The solid solutions crystallise in octahedra, frequently showing skeleton forms.

Summary.

The system $LiCl–CoCl_2–H_2O$ has been examined at 0°, 25°, 40°, and 80°, a few observations having been made also at 45° and 60°.

Three definite complex salts exist within this range of temperature : $7LiCl,2CoCl_2,18H_2O$, $3LiCl,2CoCl_2,6H_2O$, and $LiCl,CoCl_2,2H_2O$. Structural formulæ have been suggested for all of these.

There is, in addition, a remarkable series of solid solutions based upon $LiCl,H_2O$ and $2LiCl,CoCl_2,2H_2O$. The existence of these solid solutions leads, we consider, to the inevitable conclusions (i) that lithium chloride monohydrate is in reality $(LiCl,H_2O)_3$; (ii) that this polymerisation is due to instability of 1-co-ordinated lithium; (iii) that water molecules are capable of linking together the metal atoms of polynuclear kations.

THE UNIVERSITY, READING.

[*Received, March* 30*th*, 1932.]