XXV.—*Complex Formation amongst the Nitrates. Part I. The Ternary System Copper Nitrate–Cobalt Nitrate–Water.*

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NITRATO-SALTS or double nitrates have not been investigated with thoroughness. The known examples are generally confined to cases where one metal is of high atomic weight and volume, *e.g.*, $3Ni(NO_3)_2,2Ce(NO_3)_3,24H_2O$ and $2KNO_3,Ba(NO_3)_2$, although some nitrato-acids are also known. It was noticed that a mixture of copper and cobalt nitrates set to a hard mass on keeping. This phenomenon has generally been held to indicate chemical or physical reaction, whilst Hedvall and Heuberger (*Z. anorg. Chem.*, 1924, **135**, 49) and Tammann (*ibid.*, 1925, **149**, 21) have measured the rate of reaction in powdered mixtures of crystals.

The Binary Systems.

(i) *Copper Nitrate–Water.*—The hydrates of copper nitrate have been extensively studied; the anhydrous nitrate has been prepared by Ditte (*Compt. rend.*, 1879, **89**, 576, 641) and by Guntz and Martin (*Bull. Soc. chim.*, 1909, **5**, 1004). Certain complexes are known containing anhydrous copper nitrate. Funk (*Z. anorg. Chem.*, 1899, **20**, 412), from a solubility curve, inferred the existence of a nona-, a hexa-, and a tri-hydrate, and these have been generally accepted although Richards (*Amer. Chem. J.*, 1898, **20**, 706, footnote) suggested that the formula of the so-called trihydrate should be $3Cu(NO_3)_2,8H_2O$. Schreinemakers, Berkhoff, and Posthumus (*Rec. trav. chim.*, 1924, **43**, 508) showed that the hydrate crystallising from ternary mixtures of copper nitrate, ammonium nitrate, and water has the composition $Cu(NO_3)_2,2\frac{1}{2}H_2O$. This is fully confirmed in the present work and in unpublished analyses by one of the authors of the ternary system copper nitrate–silver nitrate–water; in the first case the tie-lines intersect the copper nitrate–water side of the triangle at points corresponding to 80·9, 80·8, and 80·2% $Cu(NO_3)_2$ [Calc. for $Cu(NO_3)_2,2\frac{1}{2}H_2O$: 80·6; for

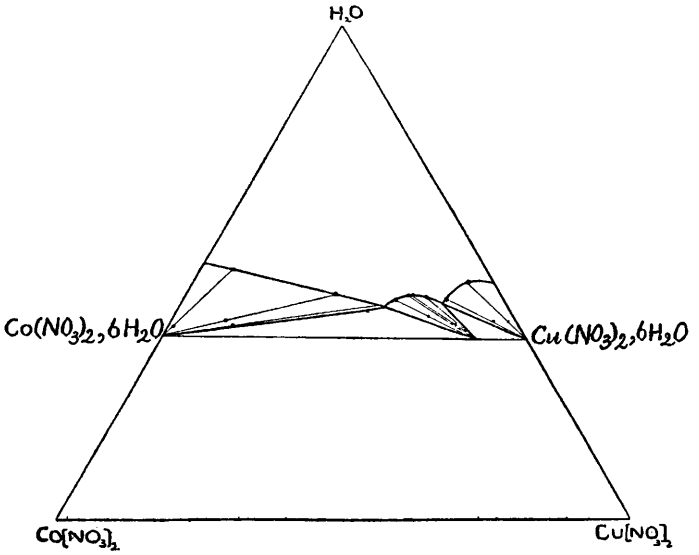
$3Cu(NO_3)_2,8H_2O$: 79·6%]. The crystals which Richards analysed were isolated from the binary system and kept over strong caustic potash solution : it is possible that they contained mother-liquor.

The solubility of copper nitrate in water at various temperatures is given in Table I as g. of $Cu(NO_3)_2$ per 100 g. of solution.

TABLE I.

Temp.	$Cu(NO_3)_2$ (%).	Hydrate present.	Temp.	$Cu(NO_3)_2$ (%).	Hydrate present.
15·0°	52·8	$6H_2O$.	30·0°	61·4	$2\frac{1}{2}H_2O$.
20·0	55·6	,,	35·0	62·0	,,
25·0	60·1	,,	40·0	62·6	,,
25·4	60·8	$6H_2O,2\frac{1}{2}H_2O$.			

FIG. 1.



Temp. 14°.

These results differ from those of Funk (*loc. cit.*), especially at the higher and lower temperatures. In addition, the temperature of the transition point is 25·4°, whereas Funk gives 24·5°—this is probably a misprint, as this point lies off his curve. Meijer (*Rec. trav. chim.*, 1924, **43**, 397), in examining the system copper nitrate–ammonium nitrate–water, obtained certain values for the solubility of copper nitrate in water, but as he failed to isolate the compound described by Schreinemakers, Berkhoff, and Posthumus (*loc. cit.*) from the same system, and as he did not question the existence of the trihydrate, it is not surprising that his solubility values depart largely from the above.

(ii) *Cobalt Nitrate–Water.*—Within the temperature limits of this investigation, this system does not call for detailed criticism: the solubilities as given by Funk (*Z. anorg. Chem.*, 1899, **20**, 412) seem to be consistently too high: the values now obtained are given in Table II, the solid phase throughout being $Co(NO_3)_2,6H_2O$.

TABLE II.

Temp.	15·0°	20·0°	25·0°	30·0°
$Co(NO_3)_2$ (%)	47·7	49·3	50·7	52·8

The Ternary System.

Three temperatures were chosen for investigation: 30°, just above the copper nitrate transition point; 20°, just below it; and 14°, at which a double salt was found to exist (see Fig. 1). This compound has the probable formula $6Cu(NO_3)_2,Co(NO_3)_2,42H_2O$,

TABLE III.

	Solution.		Residue.		
$d_{20°}^{20°}$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	Solid phase.
Temperature 14°.					
—	52·5	—	—	—	$Cu(NO_3)_2,6H_2O$.
—	47·0	5·9	60·2	1·5	,,
—	45·6	11·1	58·8	3·0	,,
—	41·5	14·0	52·8	9·4	Double salt.
—	38·9	16·0	50·2	10·8	,,
—	38·4	16·7	51·3	10·4	,,
—	36·5	19·0	47·4	12·6	,,
—	34·1	22·8	9·6	51·9	$Co(NO_3)_2,6H_2O$.
—	25·8	28·7	7·9	52·8	,,
—	5·2	44·3	1·5	59·0	,,
—	—	47·5	—	—	,,
Temperature 20°.					
—	55·6	—	—	—	$Cu(NO_3)_2,6H_2O$.
1·707	49·8	8·9	58·9	3·1	,,
—	49·4	10·8	57·8	4·9	,,
—	45·0	16·7	20·0	42·5	$Co(NO_3)_2,6H_2O$.
1·773	43·1	17·9	19·4	43·2	,,
1·705	33·7	24·5	14·8	46·7	,,
1·640	20·3	34·2	7·2	52·9	,,
1·613	13·1	38·9	3·4	56·8	,,
1·610	9·9	41·2	3·0	57·0	,,
1·598	—	49·3	—	—	,,
Temperature 30°.					
—	61·4	—	—	—	$Cu(NO_3)_2,2\frac{1}{2}H_2O$.
—	54·9	5·3	68·7	2·5	,,
—	48·4	13·0	75·9	1·9	,,
—	45·7	16·5	71·2	4·1	,,
—	37·9	22·2	9·8	52·4	$Co(NO_3)_2,6H_2O$.
—	27·1	29·2	5·6	55·5	,,
—	9·2	44·7	2·2	59·4	,,
—	—	52·7	—	—	,,

is very deliquescent, and melts at *ca.* 17°; as it is decomposed by water, its composition cannot be determined very accurately, the uncertainty corresponding to about $1H_2O$. The double salt is smoke-blue and crystallises from a magnificent purple solution.

The solutions and corresponding residues were examined in each case, and the data are in Table III.

Cobalt was determined by conversion of both metals to sulphate and electrolysis of the ammoniacal formate solution after removal of copper. Copper was determined by electrolysis of the nitric acid solution and also iodometrically: concordant results were obtained. A further check was made in the binary systems by determining both cobalt and copper as the anhydrous sulphates.

Summary.

1. The ternary system copper nitrate–cobalt nitrate–water has been examined at 14°, 20°, and 30°.

2. A complex has been isolated containing 6 mols. of the hexahydrate of copper nitrate to 1 mol. of the hexahydrate of cobalt nitrate, *i.e.*, $6Cu(NO_3)_2,Co(NO_3)_2,42H_2O$.

3. Copper nitrate "trihydrate" is shown to have the composition $Cu(NO_3)_2,2\frac{1}{2}H_2O$.

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