

The Change of Cobaltous into Cobaltic Nitrite.

By

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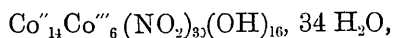
Very little is known of what happens to cobaltous nitrite when it is produced in solution in the absence of acids or dissolved salts. In 1860 the Swedish chemist, LANG, published the fact that such a solution of cobaltous nitrite left on evaporation blackish brown crystals of highly basic cobaltic nitrite (*K. S. Vet. Akad. Handl.*, 1860; *Pogg. Ann.*, 1863, **118**, 282). According to HAMPE (*Annalen*, 1863, **125**, 343), the red saline mass, thus obtained, contains cobaltous as well as cobaltic nitrite. Neither LANG nor HAMPE gave quantitative results.

In order to get LANG's crystals, precipitated calcium carbonate suspended in a very little water was dissolved up by passing in nitrous gases, cobalt sulphate in equivalent quantity was added, and the calcium sulphate filtered off. LANG and HAMPE both used barium nitrite, but the difficulty of separating barium sulphate, when precipitated from a cold neutral solution, made the use of calcium nitrite be preferred in the present research. The filtrate from the calcium sulphate was evaporated almost to dryness in a vacuum desiccator at a temperature of 30° and the

residue treated with a little water, filtered from some calcium sulphate, and left in the desiccator again to crystallise. The salt is too changeable to be safely recrystallised. It forms small very dark red crystals, very soluble in water, and remarkable for being alkaline to litmus.

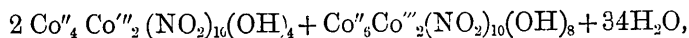
To analyse the salt, the cobalt was precipitated as cobaltous ammonium phosphate and weighed as cobaltous pyrophosphate (DIRVELL and CLARKE's process as given in DITTMAR's *Quantitative Analysis*, p. 309). The little cobalt left in solution was obtained by adding a drop of ammonium sulphide, and burning the cobalt sulphide to the black oxide, Co_3O_4 . The cobaltic cobalt in the salt was separately determined by digesting the salt with a concentrated warm solution of sodium carbonate and treating the residue twice with fresh sodium carbonate, the last time bringing the whole to boiling. The washed residue was dissolved in dilute hydrochloric acid holding potassium iodide in solution and the cobaltic estimated iodometrically. The nitrite of the salt, which had been converted by the sodium carbonate into sodium nitrite, was estimated by the permanganate method.

The results of analysis are expressed by the formula,



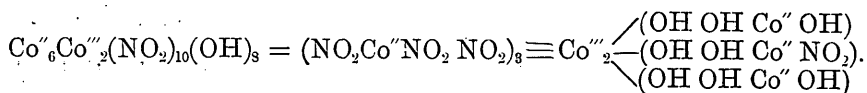
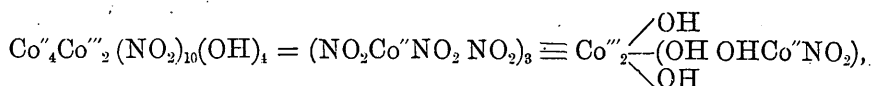
in which $\text{Co}:\text{N}=2:3$ and the ratio of the valencies of the cobalt to those of the nitrogen atoms are as slightly more than $3:2$. The tabulated percentage numbers are—total cobalt,* f. 34.13, c. 34.26; cobaltic cobalt, f. 10.42, c. 10.28; nitrogen, f. 12.31, c. 12.21.

The formula calculated for the salt is resolvable into



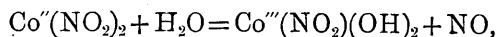
* The letters, "f." and "c." stand for "found" and "calculated."

and in other similar ways from what is known of cobaltic and other allied compounds, these constituent salts may have their formulæ expanded into the following, as probably accurate expressions of their constitution:

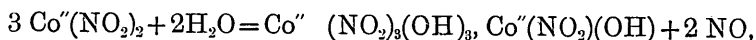


It is unnecessary to add to these formulæ the complex one for the crystalline salt as compounded of them. The apposition in them of NO_2 with NO_2 and of OH with OH serves to express, without pretending to explain, the pairing of acidic components so characteristic of such double salts as nitrites and cyanides. The NO_2 and OH groups next on either side to the Co'''_2 group represent, together with it, hemihydroxycobaltic nitrite, $(\text{NO}_2)_3\text{Co}'''_2(\text{OH})_3$, existent probably, only in combination as a double nitrite. Cobaltous nitrite and hydroxynitrite are similarly displayed in these formulæ.

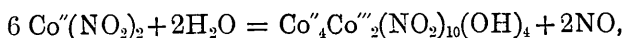
The self-conversion of cobaltous nitrite into cobaltic nitrite, merely, would be shown by the equation,



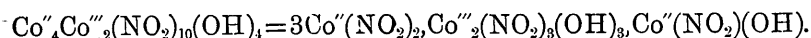
did all the cobalt nitrite ever become cobaltic, instead of but little more than one-third of it. As, however, the whole of the cobalt nitrite undoubtedly takes part in the change, this fact must be presented in the equation framed to express the conversion. This equation will be more readily followed by prefacing it with another, showing part of the change:



from which it will be seen that two cobalt atoms, in becoming cobaltic, pair together and lose only one nitroxyl group, the third cobalt atom remaining cobaltous, though also losing a nitroxyl group. The equation of the actual change is



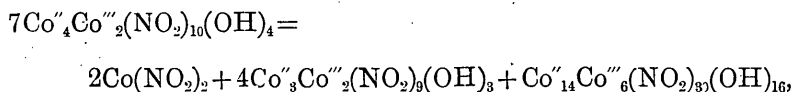
in which



That is, six molecules of cobalt nitrite become united, half of them unaltered and the other three, with loss of 2NO and acquisition of 2H₂O, as cobaltic and cobaltous hemihydroxy-nitrites. This condensation of the six molecules into a complex happens without any union taking place of the atoms of cobalt with each other through the agency of their ordinary valencies, which are, it will be seen, used up in the union of the cobalt with nitroxyl and hydroxyl atoms.

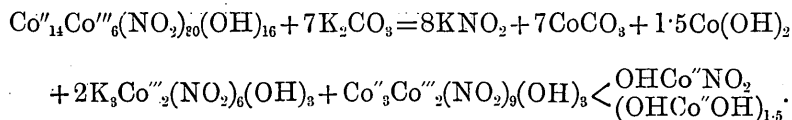
The change just formulated must be treated as indivisible, but other changes occur which may be regarded as secondary to it. There is evidently a cumulative resolution of the molecules of the $\text{Co}''_4\text{Co}'''_2(\text{NO}_2)_{10}(\text{OH})_4$ into others simpler by having given up some or all of their cobaltous hydroxynitrite and others enriched by having received this additional cobaltous hydroxynitrite. This resolution is attended with another one, that of some of the cobaltous hydroxynitrite into nitrite and hydroxide, the latter retained by the hydroxycobaltinitrite, the former lost to it by undergoing conversion itself to cobaltinitrite in a way similar to the original change. These subsidiary changes may be attributed in part to the force of crystallisation, but are principally to be referred to the feeble hold of the cobaltinitrite upon much cobaltous hydroxynitrite against the tendency of this to become itself cobaltic. The last

stage, therefore, of the conversion of cobaltous nitrite into the crystals obtained is to be expressed by



the crystalline substance, $\text{Co}''_{14}\text{Co}'''_6(\text{NO}_2)_{30}(\text{OH})_{16}$, being itself a compound of $3\text{Co}''_3\text{Co}'''_2(\text{NO}_2)_9(\text{OH})_3$ with $3\text{Co}(\text{NO}_2)(\text{OH})$ and $2\text{Co}(\text{OH})_2$.

In accordance with the remarkable constitution of the crystalline salt, indicating as it does that atoms of hydroxyl like nitroxyl groups can pair together between cobaltic and cobaltous atoms, is the behaviour of the salt when it is acted upon by half the quantity of an alkali carbonate equivalent to its cobaltous atoms. Out of 23.7 parts per cent of cobaltous cobalt present in the salt, 14.1 parts were precipitated in this way. The equation expressing this result is



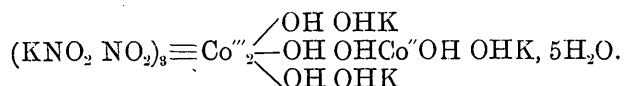
For 1.5, theory requires 2, and, since partial precipitation in this way can hardly lay claim to great accuracy, the cobaltous hydroxycobaltinitrite may allowedly be written as (p. 3)



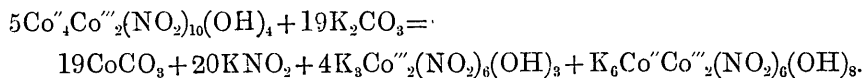
A potassium cobaltous salt is obtained by adding a solution of potassium carbonate, just so long as it continues to cause immediate precipitation, to the solution of cobaltous nitrite after its spontaneous conversion into hydroxycobaltinitrite, filtering, and gradually mixing the red-coloured filtrate with about twice its volume of absolute alcohol. The potassium cobaltous salt is thus

obtained as a rose-coloured flocculent precipitate which is very soluble in water and not stable in the air or in solution. Washed with alcohol and dried in a desiccator it was found to have the composition expressed by $K_6(NO_2)_6Co''Co'''_2(OH)_3, 5H_2O$. The calculated numbers are for this formula, after deducting $K_{0.3}$ and adding in its place $H_{0.3}$, the salt as prepared showing a deficiency of $\frac{1}{10}$ of the six atoms of potassium:—total cobalt, f. 19.56, c. 19.62; cobaltic cobalt, f. 12.82, c. 13.08; potassium, f. 24.73, c. 24.72; nitrogen, f. 9.36, c. 9.32. Only in the case of the cobaltic cobalt, and then but slightly, do the calculated numbers differ appreciably from the numbers found.

The empirical formula is remarkable in that it can be broken up into $6KNO_2 + Co_3(OH)_3 + 5H_2O$. The constitutional formula of the salt is that of a hexa-potassium hydroxy-cobaltous hydroxy-cobaltinitrite:



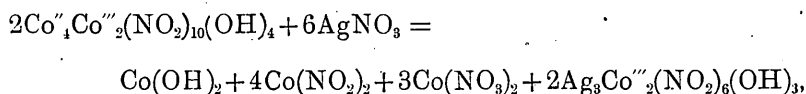
The equation satisfactorily expressing the interaction, so far as it is yet worked out, between a solution of transformed cobalt nitrite and potassium carbonate is the following:



But this equation assumes the existence of the simple potassium hydroxycobaltinitrite $(KNO_2, NO_2)_3Co'''_2(OH)_3$, which may be doubted.

With a dilute solution of silver nitrate the solution of transformed cobalt nitrite yields a straw-yellow precipitate, which is slightly soluble in water giving it an orange-yellow colour. It is unstable when moist, changing into silver nitrite and basic cobaltic

products. Its composition agrees well with the formula, $\text{Ag}_3\text{Co}''_2(\text{NO}_2)_6(\text{OH})_3$:— silver, f. 42.12 and 41.97, c. 42.13; cobalt, f. 15.61 and 15.56, c. 15.35; nitrogen, f. 10.70 and 10.66, c. 10.92. The analyses were made on different preparations of the salt. Sometimes, instead of the salt or with it, silver nitrite and cobaltic precipitates are formed. The simplest equation for expressing the interaction in which the silver hydroxycobaltinitrite is alone precipitated is :



it being understood that the cobaltous hydroxide remains in solution in combination with undecomposed hydroxycobaltinitrite, and that the cobaltous nitrite similarly combines or else proceeds to pass of itself into hydroxycobaltinitrite. The constitutional formula of the silver salt is $(\text{AgNO}_2 \text{NO}_2)_3\text{Co}''_2(\text{OH})_3$.

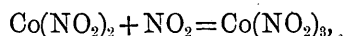
The three salts which have been obtained in this investigation of the change undergone by cobaltous nitrite in aqueous solution, namely, hydroxycobaltous hydroxycobaltinitrite, potassium hydroxycobaltous hydroxycobaltinitrite, and silver hydroxycobaltinitrite, are not the first of the hydroxycobaltinitrites which have been prepared and examined. But the method of getting these others differed from that used in the present work, in that the first step was the dissolution of cobalt carbonate in presence of water by the action of the nitrous gases from nitric acid and arsenious oxide. By taking the nitrite or carbonate of another metal with the cobalt carbonate, double salts were obtained. The salt of the other metal was taken in the proportion of three equivalents to two of cobalt carbonate, so that by passing in the nitrous gases long enough, normal cobaltinitrites could be and were thus prepared,

by ROSENHEIM and KOPPEL who introduced this method of getting cobaltinitrites and hydroxynitrites, and prepared several of them for the first time (*Zeit. anorg. Chem.*, 1898, **17**, 35). The hydroxycobaltinitrites, they obtained and analysed, were a cobaltous, a barium, a strontium, a zinc, and a silver hydroxycobaltinitrite, whilst others were met with.

It will be seen that the method followed in preparing these hydroxycobaltinitrites is not well suited for the investigation of the problem which is the subject of the present paper. For, in presence of nitrous acid and nitric peroxide, there will occur some neutralisation of basic nitrite by the former,—



and possibly some production of cobaltic nitrite from cobaltous nitrite and nitric peroxide,—

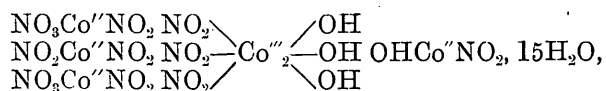


whereby the nature of the self-transformation of the cobaltous nitrite becomes obscured and the course of the change interfered with. Another objectionable feature of this mode of preparing hydroxycobaltinitrites is the production of more or less nitrate, which seems unavoidable.

In spite of the comparative unsuitability of their process from the point of view of this paper, it was necessary to repeat, if possible, some of ROSENHEIM and KOPPEL's work, the results of which were hardly consistent with those which had been got by using the LANG process. The cobaltous salt they have described was apparently indistinguishable from that now described in this paper (p. 2) except in composition. A re-examination of the cobaltous salt thus prepared was therefore decided upon.

Nitrous gases were passed into water holding cobalt carbonate

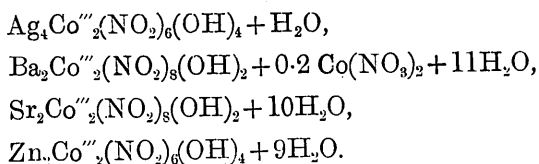
suspended until dissolution of the latter was nearly complete. The filtered solution was evaporated under reduced pressure at 30°, and yielded the expected crystals which were analysed. The results agreed well with ROSENHEIM and KOPPEL's, except that the latter did not include any finding for the cobaltic element, the proportion of it present being assumed by them to be two-fifths of the total cobalt. Calculation for $\text{Co}''_4\text{Co}'''_2(\text{NO}_2)_8(\text{NO}_3)_2(\text{OH})_4, 15\text{H}_2\text{O}$ gives figures which, with those here obtained and those found by ROSENHEIM and KOPPEL, are as follows:—total cobalt, f. 30·27, c. 29·90, Ros. f. 30·15; cobaltic cobalt, f. 9·80, c. 9·97; total nitrogen, f. 11·77, c. 11·82, Ros. f. 11·65; nitrite nitrogen, f. 9·31, c. 9·46, Ros. f. 8·90. ROSENHEIM and KOPPEL gave the salt a formula equivalent to $\text{Co}''_2\text{Co}'''_2(\text{NO}_2)_8(\text{OH})_4, \text{Co}(\text{NO}_3)_2, 12\text{H}_2\text{O}$; but this can be set aside, now that the ratio, $\text{Co}'':\text{Co}'''$ has been experimentally determined. In the light thrown upon the constitution of the hydroxycobaltinitrites by the work described in the present paper, the constitution of this nitrate-containing cobaltous salt may be expressed by



which differs from the formula given on p. 3 only in having 2NO_3 in place of 2NO_2 . But the crystals obtained from the solution prepared by LANG's method were more basic than this, and, in accordance with this difference, it was found that the crystals obtained from the solution prepared by ROSENHEIM and KOPPEL's method do not, when treated with solution of sodium carbonate equivalent to half their cobaltous element, give a precipitate containing noticeably more than half the cobaltous element. In the case of the crystals from the LANG solution, the

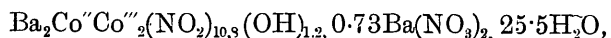
precipitate, similarly obtained, did include much more than this, though not as much as the formula indicated might have been precipitated. In that case some, in this case all, the cobaltous hydroxide remained in solution as a more basic hydroxycobaltinitrite (p. 4).

From the ROSENHEIM and KOPPEL solution the same potassium hydroxycobaltous salt and the same silver salt were obtained as from the LANG solution. In the statement on p. 7 the second analysis of the silver salt was made on a precipitate from such a solution. ROSENHEIM and KOPPEL failed to get from it anything but silver nitrite in this way, though they got a different, greyish-brown, microcrystalline, hydrated silver hydroxycobaltinitrite, indirectly through a zinc hydroxycobaltinitrite prepared in their way. To their silver salt and the other hydroxycobaltinitrites described by them, they have given formulæ equivalent to

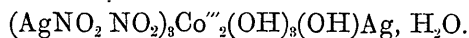


But more evidence is wanted to carry conviction as to the existence of such differences as those presented between the formulæ of the strontium and zinc salts and between the composition of ROSENHEIM and KOPPEL's series of salts and that of the salts now described. There is no evidence recorded in their paper as to whether the presence of additional nitrogen as nitrate was tested for in any other case than that of the barium salt, although in all cases the mother-liquor of the salt contained nitrate. Also evidence is wanting of the proportion of cobaltic element in the salts. As a consequence of the latter omission in the paper and by taking the more probable view that the nitrate in the barium salt

was that of barium rather than of cobalt, the formula,



can be given to their second preparation of the barium salt, and with markedly closer approximation to the results of analysis than that reached by their formula. Their silver salt, in which it is improbable that either cobaltous metal or nitrate was present, may have its given formula rearranged so as to make it appear as a derivative of the silver salt $(\text{AgNO}_2\text{NO}_2)_3\text{Co}''_2(\text{OH})_3$, here described, thus:—



It has not been found possible to get time and opportunity to extend this research by further work upon ROSENHEIM and KOPPEL's solution and its derivative hydroxynitrites or upon LANG's solution. But enough has been accomplished probably to justify the expectation that all hydroxycobaltinitrites will prove to be of the type of the salts met with in this investigation.

The author is greatly indebted to Professor T. HAGA for valuable advice given him during the course of this work and to Professor E. DIVERS, F. R. S., for assistance in expressing the significance of the results of the experiments and in preparing the text of the paper.

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