374. *Some Remarks on the Red and the Green Form of Magnus's Salt.*

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MAGNUS obtained his green salt by the action of ammonia on chloroplatinous acid, and Peyrone prepared it from $[Pt(NH_3)_4]Cl_2$ and chloroplatinous acid, thus showing that it was a chloroplatinite, $[Pt(NH_3)_4]PtCl_4$.

A rose-red form of this salt was accidentally prepared by Bjerrum. Jörgensen and Sörensen (*Z. anorg. Chem.*, 1906, **48**, **441**) showed that both the red and the green salt can result from mixing aqueous solutions of $[Pt(NH_3)_4]Cl_2$ and chloroplatinites under different conditions: production of the red form is favoured by high dilution of the solutions or by slight alkalinity (presence of a trace of ammonia), that of the green form by greater concentration or by acidity (presence of hydrochloric acid). Both salts were anhydrous, had the same composition, and were stable for several years in the dry state; but the red, although stable for some days at 97° when dry, was transformed quantitatively into the green form on being boiled with water. They noted also that the red salt could be prepared by adding the powdered tetrammino-dichloride to the dilute chloroplatinite solution.

No convincing explanation of this unique case of isomerism has yet been given. Hertel and Schneider (*ibid.*, **1931**, **202**, 77), and Cox, Pinkard, Preston, and Wardlaw (J., **1932**, 2527) examined the salts by the *X*-ray method, but reached different conclusions. The former authors found a close relationship between the two forms; but the latter workers, employing also chemical means, concluded that the red salt was indistinguishable by microscopic and *X*-ray examination from the empirically isomeric triammine plato-salt, $[Pt(NH_3)_3Cl]_2PtCl_4$, discovered by Peyrone and afterwards studied by Cleve and by Tschugaieff. On a single occasion, however, they obtained, by crystallising the green salt from hydrochloric acid, a pink orthorhombic salt which gave a green trace on rubbing; this salt was not the triammine plato-salt, though it gave almost the same *X*-ray diagram. They supposed it to be the true red form of Magnus's salt, although, in fact, the latter gives not a green but a pink trace. They state that " the supposed pink isomeride of the green salt of Magnus is usually Cleve's salt, and the true pink isomeride (or polymeride) is only occasionally formed, under experimental conditions which are not fully understood." The present work does not confirm this conclusion.

The red salt was prepared on many occasions, but in no case was it identical with the triammine plato-salt. The latter is much more soluble in water than the red form of Magnus's salt, and may easily be distinguished from it by this property; the two salts, although they have rather similar colours, are also distinct in general appearance. Chemical tests infallibly distinguish the two substances. Thus, cold aqueous sodium nitrate rapidly changes the red form into the green, but has no effect on the colour of the triammine plato-salt. Further, a lukewarm aqueous solution of $[Pt(NH_3)_4]Cl_2$ sets free the triammine from its plato-salt, the green salt of Magnus being precipitated and the triammine being found in the filtrate; whereas the tetrammine reagent is for some time without action upon the red form of Magnus's salt, and if, on heating, the latter is changed into the green salt, only the tetrammine and no triammine is found in the filtrate. Again, the following more elaborate procedure was used many times to test the various samples: the salts were powdered, and shaken in the cold with an excess of aqueous silver nitrate, silver chloroplatinite being precipitated; excess of silver was precipitated from the filtered colourless solutions of the nitrates by means of hydrochloric acid or potassium chloride; the solutions were then tested by adding aqueous potassium chloroplatinite (see Jörgensen and Sörensen, *loc. cit.*), that from the triammine plato-salt regenerating this initial salt as glittering, red, square plates soluble in hot water, whilst that from the red form of Magnus's salt gave only the insoluble rectangular needles of the green form of that salt. When potassium chloropalladite was employed instead of the chloroplatinite, the solution from the triammine plato-salt gave glistening, golden-brown, square plates of *chlorotriamminoplatinous chloropalladite,* $[Pt(NH_3)_3Cl]_2PdCl_4$ (Found: Pd + Pt, 61·0. $H_{18}N_6Cl_6PdPt_2$ requires Pd + Pt, 61·2%); whereas that from the red form of Magnus's salt gave the insoluble, greyish-pink, slender needles of $[Pt(NH)_3)_4]PdCl_4$ (Found, in dried salt: Pt, 59·0. Calc.: Pt, 59·0%). The green form of Magnus's salt gave the same result as the red form in the case of either reagent:

$$(1)\ [Pt(NH_3)_4]PtCl_4 \xrightarrow{(AgNO_3)} [Pt(NH_3)_4](NO_3)_2 \xrightarrow{(K_2PdCl_4)} [Pt(NH_3)_4]PdCl_4$$

(Green or red form of Magnus's salt.) (Greyish-pink needles.)

$$(2)\ [Pt(NH_3)_3Cl]_2PtCl_4 \xrightarrow{(AgNO_3)} [Pt(NH_3)_3Cl](NO_3) \xrightarrow{(K_2PdCl_4)} [Pt(NH_3)_3Cl]_2PdCl_4$$

(Red salt of Peyrone.) (Golden-brown square plates.)

Other considerations also show that the red form of Magnus's salt cannot be identical with or contain the triammine plato-salt, when prepared from $[Pt(NH_3)_4]Cl_2$ and a chloroplatinite. The tetrammine salt is made by dissolving one of the diammine dichlorides in excess of aqueous ammonia and allowing the strongly ammoniacal solution to evaporate. The triammine cannot survive in the presence of ammonia for more than a very short time, as was shown by direct experiments in which the authentic triammine was dissolved in water and treated with aqueous ammonia, the solution being tested at intervals. It is indeed exceedingly difficult to obtain the triammine by the action of even a limited quantity of ammonia upon a diammine, owing to the rapid conversion of the triammine into the tetrammine; and for this reason the triammine is invariably made by means of Tschugaieff's potassium cyanate method.

A cogent argument to the same effect is found also in the fact that the presence of ammonia actually favours the production of the red as against the green form of Magnus's salt when the tetrammine is treated with a chloroplatinite, whilst the presence of acid has the reverse influence; for, if the tetrammine solution actually contained triammine, ammonia would tend to change the latter into the former, whilst hydrochloric acid would tend to effect the reverse change. Cox and his co-workers employed an unusually large excess of ammonia when precipitating the red salt, and therefore the substance they obtained can scarcely have been a triammine salt.

Those authors describe an experiment in which they claim to have effected a partial conversion of the authentic red triammine plato-salt into the green salt of Magnus, by grinding the former intimately with some of the latter and then boiling the mixture with water. Using an agate mortar and pestle, and making a very intimate mixture, we failed to detect any sign of conversion on boiling with water. It seems clear that the red form of Magnus's salt has no connexion with the triammine plato-salt of Peyrone and Cleve. Indeed, if this be not so, it is difficult to understand Tschugaieff's standard method of preparing the triammine, which involves its separation as plato-salt and decomposition of this into the triammine and Magnus's green salt by treatment with the aqueous tetrammine:

$$[Pt(NH_3)_3Cl]_2PtCl_4 + [Pt(NH_3)_4]Cl_2 = 2[Pt(NH_3)_3Cl]Cl + [Pt(NH_3)_4)PtCl_4.$$

We carried out numerous preparations of the red and the green form of Magnus's salt from the tetrammine chloride or oxalate and potassium or ammonium chloroplatinite solutions. The results were in general agreement with those of Jörgensen and Sörensen (see above) as to the effect of dilution and acidity, but there were occasional puzzling exceptions, for the same solutions would at times give opposite results when mixed in the same proportion; moreover, repetitions of the same experiment might persistently give the green form and then persistently the red. We also noticed the production of intermediately coloured forms, grey or greyish-green; these, when finely powdered, could be closely imitated by mixing the powdered red and green forms in various proportions. They usually resulted under median conditions, and are doubtless mixtures of the two basic forms; sometimes fractional precipitation could be effected, the green form separating first and then the red.

The red and the green salt are closely similar in crystalline form when viewed under the microscope; their solubilities are also similar, and no difference has been detected in their chemical reactions. It is therefore highly probable that they have the same molecular weight, and it seems certain that dichroism cannot explain their occurrence.

The most interesting fresh observations made in the present experiments were: (i) that the red form can be prepared from certain chloroplatinite solutions even in the presence of concentrated hydrochloric acid; and (ii) that some of the best samples of the red form are stable for a considerable time to boiling water and even to hot hydrochloric acid; addition of a little of the green form does not seem to affect the stability. When chloroplatinous acid is prepared by dissolving platinous chloride in boiling concentrated hydrochloric acid, the filtered solution almost invariably gives rise to the red form when treated with the aqueous tetrammine; usually the crystals obtained in this way are of good colour and form, and are of exceptional stability (compare also J., **1934**, 1792). The factor which determines whether the red or the green form shall be produced may therefore reside in the condition of the chloroplatinite ion, rather than in that of the plato-tetrammine.

Although no other pair of red and green isomeric plato-salts of this kind is known, the literature contains examples of a few other green and of many other red or reddish plato-tetrammine salts. Thus, substitution of the four ammonia residues of $[Pt(NH_3)_4]PtCl_4$ by methyl-, *n*-butyl-, *iso*butyl-, or amyl-amine gives rise to a green salt in each case; but similar substitution of ethyl- or *n*-propyl-amine gives rise to a red salt. The bromoplatinite, $[Pt(NH_2Et)_4]PtBr_4$, which we prepared is, however, a green salt, so the ethylamine compounds present an interesting case.

The facts so far recorded indicate that the red and the green form of Magnus's salt are so closely related that there can be no great difference of structure; the case recalls that of the α- and the γ-form of $Pt(NH_3)_2Cl_2$. It is suggested, tentatively, that the red and the green form are electroisomerides, the difference depending upon the location of the charges.

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