375. *The Green Salt of Magnus, and Some Related Compounds.*

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So long ago as 1828 Magnus (*Pogg. Ann.*, 1828, **14**, 204) by the action of ammonia on platinous chloride, obtained a compound which is still known as Magnus's green salt. It has the empirical formula $PtCl_2,2NH_3$, but from its mode of preparation and its chemical reactions it is considered to be the complex salt $[Pt,4NH_3][PtCl_4]$. During a reinvestigation of this substance, Jörgensen and Sörensen (*Z. anorg. Chem.*, 1906, **48**, 441) noticed that under experimental conditions which should have yielded the green salt, they obtained instead a pink compound, which crystallised in scaly plates and could be changed quite easily into the green salt merely by keeping it in contact with hot water. It was established that the pink compound could be obtained by several methods, each of which, under slightly different experimental conditions, would yield the green salt. As analytical data showed that the two substances had the same empirical formula, those authors suggested that possibly the pink substance was the true complex salt $[Pt,4NH_3][PtCl_4]$, whilst the green salt was a polymeric modification. This explanation apparently did not commend itself to Werner, for in the last chapter of his " New Ideas in Inorganic Chemistry " he classifies these observations as " unexplained isomeric phenomena." In the present investigation the structure of the green salt has been elucidated by *X*-ray methods and some new results have been obtained bearing on the nature of the pink salt and its relation to the green.

The physical properties of the two salts had not been investigated previously with any degree of completeness. Both are described as crystallising in the tetragonal system, apparently without adequate justification. Recently, Hertel and Schneider (*Z. anorg. Chem.*, 1931, **202**, 77) have made an *X*-ray examination of the two forms by the powder method, and conclude that they are tetragonal with almost identical lattices. The more detailed investigation now reported shows that their interpretation of the *X*-ray photographs is incorrect.

Crystallography and Structure of the Green Salt.—This salt forms small elongated rectangular crystals which show straight extinction, high refringence, and strong dichroism. Crystals can sometimes be obtained large enough to be observed endwise; these all have a square cross-section and show a uniform interference colour at all positions between crossed Nicols. Some also are large enough to show a uniaxial cross in convergent light, which, however, is not sufficiently well defined to enable a determination of optic sign to be made or to exclude with absolute certainty the possibility of its being a biaxial figure of very small optic axial angle. These results indicate that the crystals are probably tetragonal combinations of {100} and {001}; this is confirmed by the *X*-ray examination. From the fact that the crystals do not extinguish between crossed Nicols when viewed along the *c*-axis, it is concluded that they are optically active. (The alternative explanation would be that they are lamellar twins of lower symmetry, but there is nothing whatever to suggest this in the appearance of the crystals.) The crystals are too small to enable quantitative observations to be made on the rotation, or to observe its effect on the interference figure in convergent light. The refractive indices are too high ($>$1·75) to be measured by the immersion method, but the relief shown in methylene iodide indicates that ε is greater than ω. The extraordinary ray is strongly absorbed, and gives the crystals the dark green colour, while the absorption of the ordinary ray is much less, so small crystals appear almost colourless when viewed through (001). Crystals are sometimes observed which have apparently commenced to redissolve after formation, with the result that the ends are tapered. In no case have such crystals been observed to show symmetrical tapering at both ends; frequently one end is considerably eroded while the other is unaffected. This indicates that the *c*-axis is polar, so that, the optical activity being taken into account, the crystals presumably belong to the C_4 class (tetragonal polar).

An *X*-ray examination has been made by the single-crystal and the powder method. It is difficult to obtain satisfactory Laue photographs of the crystals, but the rotation photographs show that they are tetragonal in agreement with the microscopic examination. From rotation photographs, the cell dimensions are found to be $a = 6·29$, $c = 6·42$ Å.U., both ± 0·02 Å.U., so that with one molecule of $[Pt,4NH_3][PtCl_4]$ in the unit cell, the calculated density is 3·90 g./c.c. (Found : 3·3—4·1). If, as suggested above, the crystal class is pyramidal, the space-group is C_4^1 (*P*4). The fact that there is only one molecule in the cell disposes at once of any idea of polymerisation in the ordinary sense.

The main lines of the structure are immediately suggested by the nature of the *c*-axis rotation photograph. The first and third layer lines are almost entirely missing, showing that along the *c*-axis almost identical scattering units alternate at intervals of *c*/2. These groups are clearly $[PtCl_4]$ and $[Pt,4NH_3]$ ions, which have similar scattering powers and are known from previous work (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404; Cox, this vol., p. 1912) to have the same configuration. A platinum atom in the anion being placed at (000) in the unit cell, the platinum atom in the kation is at the point (00$\frac{1}{2}$). It now remains to establish the position of the four chlorines and the four ammonias.

Since there is no reason to suppose that the two complex ions differ in any way from those in K_2PtCl_4 and $Pt(NH_3)_4Cl_2$, it might be assumed that they have the same configuration (*i.e.*, planar) in this case as in the substances mentioned. That this is actually the case is shown by the following considerations. The intensities of the even orders of (001) fall off regularly with increasing glancing angle, while the odd orders, as far as can be observed (up to the 7th), are absent. In addition, the (002) reflexion is stronger than any other observed. These results indicate that practically all the scattering matter in the cell is concentrated in the (002) planes. For example, a simple calculation shows that if the chlorines and ammonias were displaced out of the (002) plane by 0·5 Å.U., the (005) reflexion would be nearly as strong as the (006). Thus the displacement, if any, must be considerably less than this, and in the absence of quantitative intensity measurements it can be said that all the atoms lie in the (002) planes. Since the ions must have tetragonal symmetry, it follows that they must have the same configuration as in previous cases; the platinum atom is at the centre of a square formed by four chlorine atoms or four ammonia groups.

Four quantities now suffice to determine the structure completely (except for the position of hydrogen atoms). These are the distances Pt–Cl and $Pt–NH_3$, and the angles which the directions of these bonds make with the *a*-axis. These can only be determined accurately by precise intensity measurements which would be difficult to make with such small and highly absorbing crystals, but by assuming the first two, and making use of the principle that the co-ordination number (in the crystallographic sense) of each atom or group will tend to be as high as possible, giving an arrangement of minimum potential energy, the two angles can be calculated and a structure found. The essential correctness of the result is shown by the complete qualitative agreement between experimental and calculated intensities.

Since the two ions have the same configurations as in K_2PtCl_4 and $Pt(NH_3)_4Cl_2$, it will be assumed that the distances Pt–Cl and $Pt–NH_3$ remain the same. These distances are 2·32 and 2·62 Å.U. respectively (Dickinson; Cox, *locc. cit.*). Now the most symmetrical structure possible is that shown in Fig. 1, which gives a projection of the unit cell on (001). [The $Pt(NH_3)_4$ groups are at a depth $c/2$ below the $PtCl_4$ groups.] Although the most symmetrical, this is evidently not the most stable structure, since each Cl atom (or NH_3 group) is surrounded by only four of the other kind, and is in contact with one of the same kind. If, however, the ions are rotated about the c-axis through a suitable angle, the arrangement is such that each atom or group is surrounded at almost equal distances by *six* of the other kind. This angle, with the assumed interatomic distances, is 30°, and the resulting structure is shown in Fig. 2. That this structure is correct in essentials is shown by Table I, which gives the observed qualitative intensities, I, for the more important planes in the c-zone, together with those calculated (in arbitrary units) from the atomic positions of Fig. 2, using the atomic scattering factors given by James and Brindley (*Z. Krist.*, 1931, **78**, 470). It will be seen that the agreement is quite satisfactory.

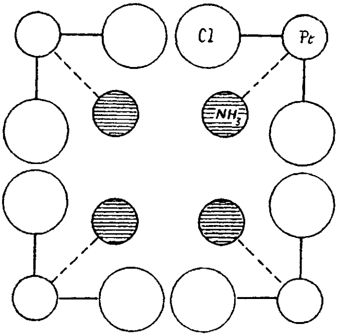

FIG. 1.

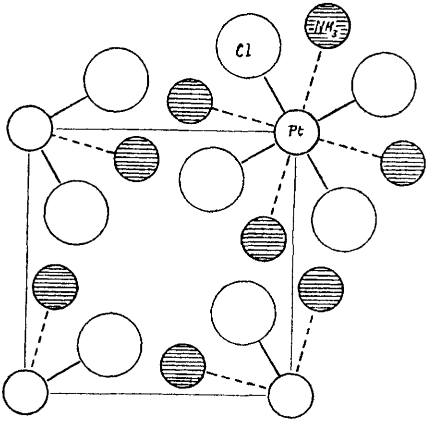

FIG. 2.

TABLE I.

hkl.	I (obs.).	I (calc.).
110	strong	12
200	moderate	9
210	very strong	19
220	very strong	18
300	strong	11
310	very strong	22
400	moderate	6

The structure also agrees with the low symmetry deduced from the microscopic observations; the arrangement of the ions to give the required stability destroys the vertical planes of symmetry, while if the NH_3 groups are not rotating there can be no horizontal plane, so that only the four-fold axis remains. The fact that the results for $Pt(NH_3)_4Cl_2$ (Cox, *loc. cit.*) require the NH_3 groups to be rotating, whereas in the present case apparently they are not, may probably be explained in the following way. In the tetrammine each NH_3 is surrounded symmetrically by four Cl ions in a plane perpendicular to the Pt–NH_3 bond, so that the field of force around it may be almost radially symmetrical, whereas in the case under consideration the NH_3 is surrounded by six only approximately equidistant Cl atoms which themselves cannot have the practically spherical symmetry of the Cl ions in the tetrammine. Thus we can readily imagine that in the tetrammine the potential energy of the NH_3 group is nearly independent of its angular position, so that rotation is possible, whereas in the plato-salt there are fairly well-defined minima in the energy values and the group is confined to the angular positions corresponding to these minima. It is to be expected that at a sufficiently high temperature the oscillations of the group about the stable position will pass into complete rotation. This should be accompanied by loss of polarity and optical activity. In this connexion it may be pointed out that in cases where group-rotation can occur, caution may be necessary in using the liquid-air test for pyroelectricity (Martin, *Phil. Mag.*, 1931, **22**, 519), since it is conceivable that a substance which is non-polar under normal conditions may become polar before liquid-air temperature is reached owing to the transition of the groups from rotational to non-rotational states.

The insolubility and unusual colour of the green salt have been ascribed to polymerisation; although this is not the explanation, there is a possibility that the lattice is not a simple ionic one like that of, *e.g.*, K_2PtCl_4, but has a very slight tendency to the layer (*e.g.*, CdI_2) type. The fact that the green colour is shown chiefly by the extraordinary ray (vibrating parallel to the symmetry axis) indicates that it is due, not to any peculiarity in the structure of the ions themselves, but rather to the manner in which they are linked together and to their distorting effect on each other in the direction of the *c*-axis. Now, if the possibility of four coplanar nitrogen valencies is excluded, the three hydrogens on each nitrogen cannot be distributed symmetrically with respect to the six surrounding chlorine atoms, and therefore a given kation cannot be related quite equally to the anions on either side of it. The effect of this is probably manifested principally in the unsymmetrical deformation of the chlorine atoms; it is insufficient to cause any displacement of the ions bodily with respect to each other. Although the positions of the hydrogen atoms are evidently of considerable importance in this connexion, any attempt to establish them must be purely speculative, since the *X*-ray method gives no information on the matter.

Apart from the satisfactory agreement between observed and calculated *X*-ray intensities, a further check on the correctness of the structure is afforded by the calculation of the distances between the Cl atoms and the NH_3 groups. In the present structure each NH_3 group is at a distance of 3·74 Å.U. from four chlorines, and 3·68 Å.U. from two. On the basis of previous results (for K_2PtCl_4 and $[Pt,4NH_3]Cl_2$) the distance should be 3·55 Å.U. It is not to be expected that the agreement should be exact, on account of the deformability of the Cl atoms; the difference in colour between the chloroplatinite and the plato-salt indicates that the deformation of the anion is not the same in the two cases.

The structure now proposed may be described briefly by means of the cell dimensions and atomic co-ordinates as follows. Cell dimensions: $a = 6{\cdot}29$, $c = 6{\cdot}42$ Å.U.; atomic co-ordinates: Pt, (0, 0, 0) and (0, 0, $\frac{1}{2}$); Cl, $\pm (u, v, 0)$ and $\pm (v, -u, 0)$; NH_3, $\pm (p, q, \frac{1}{2})$ and $\pm (q, -p, \frac{1}{2})$. The values of the parameters are $u = 0{\cdot}18$, $v = 0{\cdot}32$, $p = 0{\cdot}40$, and $q = 0{\cdot}11$. Apparently no structure of this type has been described previously.

The palladium analogue of the green salt of Magnus, the pink $[Pd,4NH_3][PdCl_4]$ (cf. Drew, Pinkard, Preston, and Wardlaw, this vol., p. 1895), has also been examined. The crystals are much smaller than those of the salt of Magnus, but are very similar in appearance. *X*-Ray powder photographs of the two are almost identical, in both the position of the lines and their relative intensities. It is therefore highly probable that the palladium compound has the same structure as the salt of Magnus. This result is in complete agreement with the conclusion from the chemical evidence that this substance is a tetrammine plato-salt and not a diammine.

Crystallographic and X-*Ray Examination of the Pink Salt of Magnus.*—The pink salt is never obtained quite free from the green. It is precipitated sometimes as an extremely fine powder, and sometimes in very thin square plates, irrespective of the method of preparation. With one exception, the crystals were indistinguishable by microscopic and *X*-ray examination from the triammine plato-salt $[Pt,3NH_3,Cl]_2[PtCl_4]$ (Cleve's salt), which has the same empirical formula as the salt of Magnus. This substance forms thin pink tetragonal plates, showing a positive uniaxial figure in convergent light. *X*-Ray rotation photographs showed the length of the *c*-axis to be 8 Å.U. approx.

In the one exceptional case, the salt, which was obtained by the action of hydrochloric acid on the green salt, formed pink plates, which in ordinary light were almost indistinguishable from the triammine plato-salt, but in polarised light showed straight extinction and gave no interference figure. The crystals showed a further difference in that they left a distinct green trace on rubbing. An *X*-ray examination by the single-crystal rotation method showed the substance to be orthorhombic with cell dimensions $a = 7{\cdot}9$, $b = 8{\cdot}2$, $c = 7{\cdot}9$ Å.U. (*c*-axis normal to the plates). With two molecules of $[Pt,4NH_3][PtCl_4]$ to the unit cell, the calculated density is 3·9 g./c.c., *i.e.*, the same as the green salt. One, two, or more molecules of $[Pt,3NH_3,Cl]_2[PtCl_4]$ would give impossible densities. This substance is therefore the true pink salt of Magnus. That it is, however, very closely related to the triammine plato-salt is shown by the extremely close similarity between their *X*-ray photographs. The *c*-axes of the two are equal, and the *a*-axis of the triammine salt is probably 3 or $3/\sqrt{2}$ times that of the tetrammine salt.

Thus 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 yet fully understood. (The very fine pink powder which is sometimes precipitated may be either substance, since the two *X*-ray powder photographs are too nearly the same to enable a certain distinction to be made.) The triammine plato-salt formed in this way is probably not perfectly pure, since it differs from the pure substance obtained by the usual method (Tschugaev, J., 1915, **107**, 1247) in its solubility and stability. The pure salt can be recrystallised without much difficulty from water, whereas that from Magnus's salt is less soluble and usually changes to the green on boiling. This suggests that it contains, probably in solid solution, a small amount of green salt, and that on heating it becomes unstable and is converted almost entirely into the green. This conclusion is supported by the fact that the colour of the pink salt is not absolutely constant from one specimen to another; it was further tested by mixing very intimately some authentic triammine plato-salt with a little green salt in a mortar, and then boiling them with water. It was found that the resulting solution, after filtration of undissolved green salt, deposited after a time an appreciable further quantity of green, the total amount being greater than had been used originally. Very little pink crystallised unchanged. It therefore seems that any apparent chemical differences between the triammine salts obtained by the two methods can be explained by the presence of green salt of Magnus in the one case. It should be noted that owing to its very high insolubility in water, the green Magnus salt must be in very close contact with the Cleve salt to make it unstable; the presence of the green salt as separate crystals is not sufficient.

There is insufficient evidence at present regarding the structures of the triammine plato-salt and the pink salt of Magnus to enable any useful speculation to be made regarding the relation of these substances to each other or to the green salt. The orthorhombic pink salt may be a dimeric form, although it is difficult to see how a comparatively simple ionic compound like the green salt of Magnus can polymerise and at the same time become more soluble. Its lower symmetry and instability suggest that the pink is possibly a form in which the ions have lost their planar configuration. If, as seems possible, the transformation from Cleve's salt to Magnus's salt takes place by the interchange of co-ordinated groups between anions and kations, the ions of the Magnus salt would temporarily have a non-planar configuration, and thus the pink salt may well be this unstable form intermediate between the other two.

The results recorded above show that the deductions of Hertel and Schneider (*loc. cit.*) are almost entirely incorrect. They give the cell dimensions as $a = 6{\cdot}3$, $c = 5{\cdot}15$ Å.U. for the green, and $a = 6{\cdot}3$, $c = 5{\cdot}25$ Å.U. for the pink salt, which only agree with the present results in the value for the green a-axis. The densities from the above cell-dimensions are approx. 4·7 g./c.c., which is also definitely wrong. It is unfortunate that Hertel and Schneider do not give the values of their experimental densities or state how they were determined. These errors indicate the caution which is necessary in applying the powder method alone to any but the simplest structures. The powder photographs obtained in the present work agree with those of Hertel and Schneider, but they can, of course, be interpreted by means of the cell-dimensions obtained from the single-crystal photographs.

EXPERIMENTAL.

Tetramminoplatinous dichloride, $[Pt,4NH_3]Cl_2$, prep. from α- or β-diamminoplatinous dichloride and NH_3 aq., formed colourless needles or prisms of the monohydrate. With aqueous K_2PtCl_4 free from K_2PtCl_6, it gave generally the green salt of Magnus.

To prepare the pink salt we used, at first, the elaborate method described by Jörgensen and Sörensen (*loc. cit.*), but later obtained better results by a much simpler process. An aq. solution of $[Pt,4NH_3]Cl_2$ was made, and to it 0·25 of its vol. of NH_3 aq. (d 0·88) was added. On addition of a neutral soln. of pure K_2PtCl_4, the pink salt was deposited in good yield, with a small quantity of green.

Whilst recrystallising green Magnus salt from HCl aq., it was found that by using certain concns. of acid and solute, a pink compound could be prepared, which on examination proved to be the same as that obtained by the other methods. About 0·2 g. of Magnus's salt was added to 150 c.c. of HCl (*ca.* $2N$). The mixture was heated until all the green salt had dissolved, and then filtered twice to remove any remaining traces of the green, and allowed to cool. The resulting crystals were chiefly pink, mixed with a little green.

Determination of Densities.—The densities could not be determined by the specific gravity bottle owing to the small amount of material available. Both the pink and the green salt of Magnus and Cleve's salt sink in CH_2I_2 (d 3·3). An aq. soln. of Tl formate was made so that a crystal of celestine (d 3·96) just floated and one of barytes (d 4·48) sank in it. From the proportion of the celestine crystal submerged, the density of the solution was estimated to be not more than 4·1 g./c.c. Crystals of the green salt floated on this, so their density is definitely less than 4·1. The pink salt could not be tested in this way since it turned green when put into the solution which was necessarily hot to give the required density. From its rate of sedimentation in CH_2I_2, however, it appears to have approx. the same density as the green salt.

Summary.

(1) The conditions for the preparation of the green and the pink salt of Magnus have been reinvestigated.

(2) The crystalline structure of the former has been determined by *X*-ray investigation. It is shown not to be a polymerised substance. The ions $[PtCl_4]$ and $[Pt,4NH_3]$ have the same form as in K_2PtCl_4 and $[Pt,4NH_3]Cl_2$, except that the ammonia groups in the kation are not rotating.

(3) An orthorhombic pink salt of Magnus has been found to exist, but the pink salt commonly obtained is actually Cleve's salt, $[Pt,3NH_3,Cl]_2[PtCl_4]$. Both the true pink salt of Magnus and Cleve's salt are convertible into the green salt.

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