# *Nuclear Magnetic Resonance Spectra and the Structure of Infusible White Precipitate.*

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Proton magnetic resonance spectra are given for samples of infusible white precipitate prepared by three different methods, and for a sample of fusible white precipitate. The results support the structure $NH_2\cdot HgCl$ for infusible white precipitate and exclude the structures $NHg_2Cl,NH_4Cl$ and $xHgO,(1-x)HgCl_2,2NH_3$. It is suggested that preparations of infusible white precipitate may often contain impurities of mercuric chloride, of fusible white precipitate, or of $xHgO,(1-x)HgCl_2,2NH_3$, according to the conditions.

Gmelin–Kraut's " Handbuch der anorganischen Chemie " lists the formulæ of some twenty compounds which have been thought to be formed by the interaction of mercuric chloride and ammonia solutions. The structure of one of these, namely " infusible white precipitate," has been investigated by many workers during the past century. It has been formulated by Rammelsberg (*J. pr. Chem.*, 1888, **38**, 558) as $NHg_2Cl,NH_4Cl$ (I), by Franklin (*J. Amer. Chem. Soc.*, 1907, **29**, 35) as $NH_2\cdot HgCl$ (II), and by Britton and Wilson (*J.*, 1933, 601, 1045) as $xHgO,(1-x)HgCl_2,2NH_3$ (III). Quantitative chemical analysis has not provided unambiguous evidence in favour of any one of these structures.

Samples of infusible white precipitate have been prepared by various methods, and their proton magnetic resonance spectra observed. The shapes and mean-square widths of these spectra depend upon the grouping and internuclear separation of the hydrogen atoms (see, *e.g.*, Purcell, *Science*, 1948, **107**, 433; Pake, *Amer. J. Physics*, 1950, **18**, 438, 473; Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261; Smith, *Quart. Reviews*, 1953, **7**, 279), and thereby provide a method of distinguishing between structures (I), (II), and (III).

Rammelsberg's formula (I) was put forward as part of a scheme which formulated many of the mercuric chloride–ammonia compounds as double salts of ammonium chloride. Franklin's formula (II) was supported by Hofmann and Marburg (*Annalen*, 1899, **305**, 191) on the basis of experiments in which the actions of silver nitrate and of calcium hydroxide on the precipitate were investigated quantitatively.

In 1933 Britton and Wilson (*loc. cit.*) suggested formula (III) on the basis of conductometric and electrometric titrations of mercuric chloride and aqueous ammonia. This formula has recently received further support from Glasson and Gregg (*J.*, 1953, 1493) who measured the rate of thermal decomposition and the dissociation pressure of infusible white precipitate, and compared the activation energy of the reaction with those of the decomposition of compounds of known formulæ. They also measured the loss in weight due to the elimination of ammonia and found the results to be consistent with formula (III).

Lipscomb (*Acta Cryst.*, 1951, **4**, 266) interpreted *X*-ray diffraction patterns of infusible white precipitate in terms of long chains of alternate mercury atoms and $-NH_2^+-$groups, with the chloride ions packed between the chains. An analogous structure has also been found for the corresponding bromide (*idem, ibid.*, 1952, **5**, 604).

The diversity of these conclusions may be due partly to the different methods of preparation used. Thus, whereas Franklin used the action of liquid ammonia or of sodamide on solid mercuric chloride, Lipscomb used 0·685N-ammonia solution and mercurous chloride, Britton and Wilson used 0·1027N-ammonia solution and 0·025M-mercuric chloride solution, and Glasson and Gregg used the methods of the British Pharmacopœia (1914).

## Experimental

(a) *Preparation of Samples.—Infusible white precipitate, sample A.* A solution of 60 g. of " AnalaR " mercuric chloride in 1200 c.c. of water was run slowly into 480 c.c. of N-ammonia solution, with stirring. The precipitate was washed with a small quantity of water and dried at 30°. Analysis of the mercury content by precipitation as $Cu(en)_2HgI_4$ (Vogel, " Quantitative Analysis," Longmans, London, 1943, p. 505), where en represents ethylenediamine, the chlorine as silver chloride, and the nitrogen by Kjeldahl's method gave Hg, 78·7; Cl, 16·7; $NH_3$, 4·93% (Calc. for $HgNH_2Cl$: Hg, 79·6; Cl, 14·1; $NH_3$, 6·8%. Calc. for $0{\cdot}25HgCl_2,0{\cdot}75HgNH_2Cl$: Hg, 78·0; Cl, 17·2; $NH_3$, 5·0%). If left in contact with water, the precipitate becomes yellow, probably owing to the formation of $Hg_2ONH_2Cl$ (Brauer, " Handbuch der Preparativen anorganischen Chemie," Ferdinand Enke Verlag, 1951, Vol. 6, p. 824).

*Infusible white precipitate, sample B.* This was prepared as for sample A, but with use of 3N-ammonia solution (Found : Hg, 77·4; Cl, 13·8; $NH_3$, 7·0%).

*Infusible white precipitate, sample C.* A small amount of sample A was dissolved in "AnalaR" ammonia solution (*d* 0·88) (Saha and Chouhudri, *Z. anorg. Chem.*, 1910, **67**, 357) and then allowed to crystallise slowly in a vacuum-desiccator over concentrated sulphuric acid. The yield was very small, but the product was crystalline.

*Fusible white precipitate,* $HgCl_2,2NH_3$. Alexander's method (Reaktionen von Salzen in Aethyl Acetat, Diss., Giessen, 1899, 9) as used by Palmer (" Experimental Inorganic Chemistry," C.U.P., 1953) was adopted, in which a stream of dry ammonia was passed into a solution of mercuric chloride in anhydrous ethyl acetate.

The analyses quoted above are probably not very reliable as the results appear to vary with the method used (Lipscomb, *Analyt. Chem.*, 1953, **25**, 737). The mercury and chlorine analyses were internally consistent but it was difficult to get reproducible results for the ammonia estimation. Similar difficulties have been reported by Brodersen and Rüdorff (*Z. anorg. Chem.*, 1954, **275**, 141).

(b) *Nuclear Resonance Measurements.*—The apparatus used has already been described (Richards and Smith, *loc. cit.*; Pratt and Richards, *Trans. Faraday Soc.*, 1953, **49**, 744). The radio-frequency coil is made of bare silver wire wound internally in a fired soapstone former. The sealed glass tube containing the sample fits snugly into the coil. Measurements on an empty sample tube have shown that the coil and former give no proton resonance signal.

The nuclear resonance spectrometer produces a record of the first differential of the absorption line, and the absorption line itself is obtained by numerical or graphical integration of the experimental record. The broadening or width of the adsorption line is expressed in terms of the mean-square width, or second moment in gauss². The second moment ($\Delta H_2^2$) is given by

$$\int_{-\infty}^{+\infty} f(H) \, . \, H^2 dH \Big/ \int_{-\infty}^{+\infty} f(H) \, . \, dH$$

where f($H$) is the line shape function, and $H$ is the distance in gauss from the centre of the line. Line widths can readily be expressed in frequency units instead of magnetic field units by means of the relation $h\nu = \mu H/I$, where $h$ is Planck's constant, $\nu$ is the frequency, $\mu$ is the nuclear magnetic moment, $I$ the nuclear spin quantum number, and $H$ the magnetic field strength.

The samples were all studied at 90° K in liquid oxygen, and sample A and the fusible white precipitate were also measured in liquid hydrogen at 20° K.

*Results.*—The proton resonance spectra at 90° K are shown in Figs. 1—4, which show for each sample a typical experimental derivative curve and the integrated absorption curve. The double-ended arrows represent the magnetic field modulation used. The spectrum of sample A at 20° K was identical with that at 90° K, but the spectrum of fusible white precipitate at 20° K was broader than at 90° K and resembled an incompletely broadened line due to an equilateral triangular group of protons. The points superimposed on the absorption curves are calculated ones which will be referred to in the discussion.

The second moments of the curves obtained at 90° K, and the line widths (expressed as the separation of the outer maxima of the derivative curves) are given in the Table below together with their standard deviations.

| | Second moment, gauss² | Line width, gauss | Number of runs taken |
|---|---|---|---|
| Sample A .................. | 18·3 ± 1·0 | 10·7 ± 0·3 | 11 |
| B .................. | 18·6 ± 1·1 | 11·4 ± 0·2 | 8 |
| C .................. | 20·25 ± 1·5 | 11·7 ± 0·6 | 6 |
| Fusible white precipitate | 10·2 ± 0·7 | 3·85 ± 0·15 | 4 |

The signal obtained from sample C was weak, since only a small amount was available and so the second moment obtained may be less reliable than in the other cases.

FIG. 1. *Infusible white precipitate, sample A.—Derivative and absorption curves at* 90° K. *Dots represent points calculated for pairs of protons,* 1·688 Å *apart* ($\alpha = 3\mu/2r^3 = 4{\cdot}4$ *gauss*) *with a broadening function* $\beta^2 = 3{\cdot}6$ *gauss*$^2$.

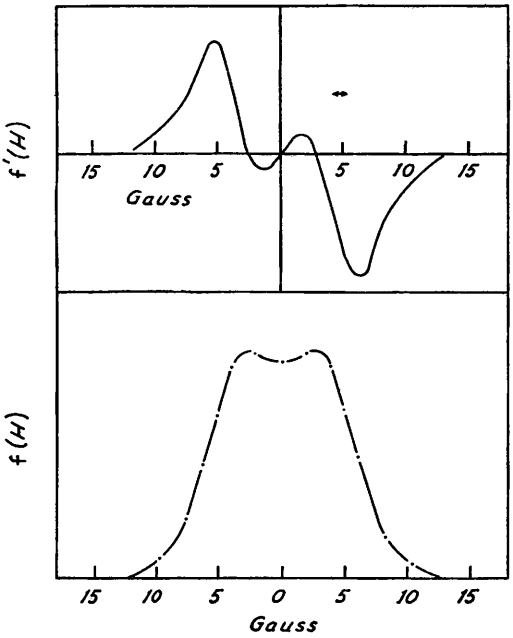


FIG. 2. *Infusible white precipitate, sample B.—Derivative and absorption curves at* 90° K. *Dots are calculated for a mixture of* $NH_2{\cdot}HgCl$ *and* $HgCl_2,2NH_3$ *in ratio* 0·84 : 0·16.

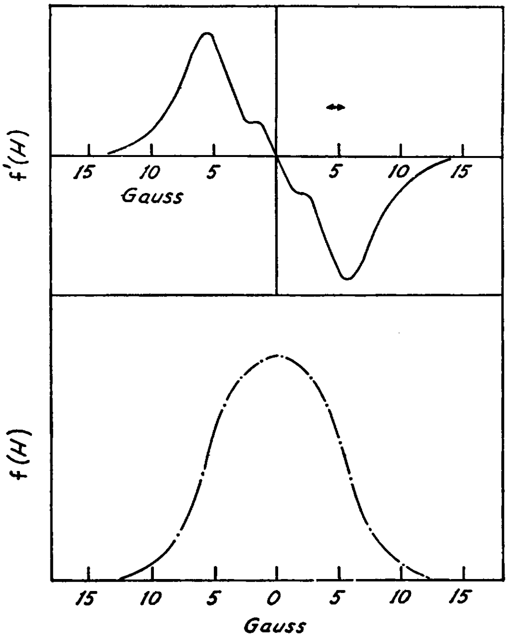


FIG. 3. *Infusible white precipitate, sample C.—Derivative and absorption curves at* 90° K. *Dots represent points calculated for pairs of protons* 1·688 Å *apart* ($\alpha = 3\mu/2r^3 = 4{\cdot}4$ *gauss*) *with a broadening function* $\beta^2 = 3{\cdot}6$ *gauss*$^2$.

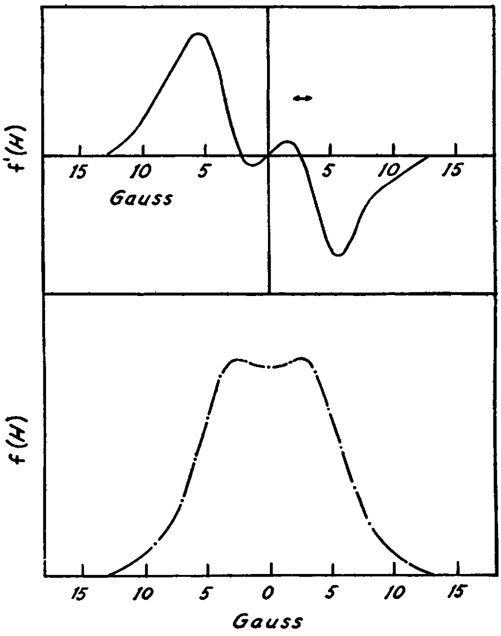
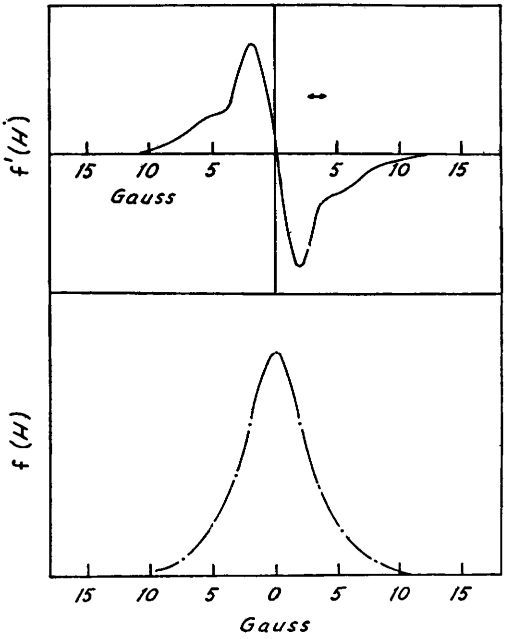


FIG. 4. *Fusible white precipitate.—Derivative and absorption curves at* 90° K. *Dots are calculated for equilateral triangle of protons* 1·682 Å *apart rotating about an axis perpendicular to their plane,* $\alpha = 4{\cdot}442$ *gauss and* $\beta^2 = 3{\cdot}5$ *gauss*$^2$.



## DISCUSSION

In structure (I; $NHg_2Cl,NH_4Cl$) the hydrogen atoms are arranged in tetrahedral groups, in (II; $NH_2{\cdot}HgCl$) they are grouped in pairs, and in [III; $x$HgO,(1 − $x$)$HgCl_2,2NH_3$] they are arranged at the corners of equilateral triangles. The proton resonance line shapes and their approximate second moments for these three rigid arrangements of protons are shown in Fig. 5 (Andrew and Bersohn, *J. Chem. Phys.*, 1950, **18**, 159). If appreciable molecular motion occurred in the solids, these lines would be considerably narrowed (Gutowsky and Pake, *J. Chem. Phys.*, 1950, **18**, 162), but the one for structure (II) would retain its shape.

*Infusible White Precipitate, Sample A.*—The shape of the experimental curve fits that expected for formula (II), and its second moment (18·3 gauss$^2$) is as expected. As the line remained unchanged between 20° K and 90° K it may be assumed to be due to a rigid structure at 90° K. In Fig. 1 the dots represent points calculated theoretically (Pake, *ibid.*, 1948, **16**, 327) for the absorption line of pairs of protons, 1·688 Å apart, broadened by a Gaussian function of mean-square width 3·6 gauss$^2$. This inter-proton distance corresponds to an N–H distance of 1·03 Å, if the HNH angle is tetrahedral, as seems likely from the $X$-ray measurements (Lipscomb, *Acta Cryst.*, 1951, **4**, 266). The N–H distance in the ammonium ion is 1·03 Å (Levy and Peterson, *Phys. Review*, 1952, **86**, 766). The width of the absorption line depends upon the inverse cube of the H–H distance. The second moment of the calculated line, which depends on the inverse sixth power of the H–H distance, is 19·1 gauss$^2$ compared with 18·3 gauss$^2$ found.

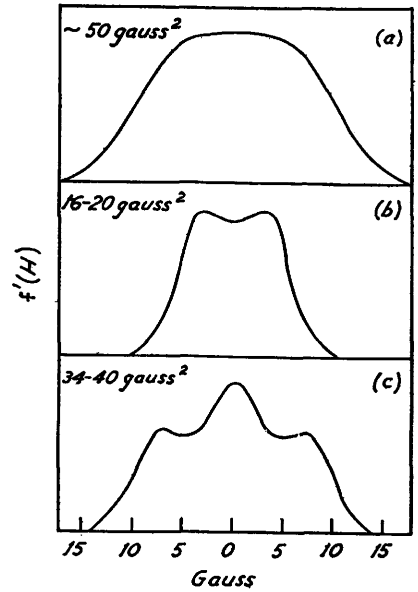


FIG. 5. *Absorption curves expected for different structures.*—(a) *Tetrahedral groups.* Rammelsberg, $NHg_2Cl,NH_4Cl$. (b) *Pairs.* Franklin, $NH_2{\cdot}HgCl$. (c) *Triangles.* Britton and Wilson, $x$$H_2O$,(1 − $x$)$HgCl_2,2NH_3$.

These results show conclusively that the protons in sample A are arranged in pairs, and this gives very strong support to structure (II). Fig. 5 shows that the other structures would give very different line shapes and second moments. Sample A may, however, contain other impurities which do not contain hydrogen atoms, because such impurities would make no contribution to the proton resonance spectrum. The analysis suggests the presence of mercuric chloride which is probably co-precipitated with the infusible white precipitate. Broderson and Rüdorff (*Z. anorg. Chem.*, 1954, **275**, 141) find that mercuric bromide is co-precipitated in the preparation of $NH_2{\cdot}HgBr$ when ammonia solution of concentration greater than 0·09N is used, and have shown that mixed crystals of $NH_2{\cdot}HgBr$ and $HgBr_2$ are formed.

*Infusible White Precipitate, Sample B.*—As this sample was prepared from more concentrated ammonia solution than A, it is possible that the formation of mercuric chloride diammine is facilitated. The analysis of this sample is consistent with this view. If this is correct, its proton resonance spectrum would be expected to be a superposition of that of infusible white precipitate and of fusible white precipitate in the appropriate proportions. The absorption line of fusible white precipitate at 90° K, obtained experimentally, is shown in Fig. 4 and discussed below. The dots in Fig. 2 represent points obtained by superposing the experimental absorption curves of sample A (Fig. 1) (which is due only to the infusible white precipitate, any mercuric chloride impurity making no contribution to the signal) and of fusible white precipitate (Fig. 4), in such a way that their areas are in the ratio of 0·84 : 0·16 respectively. The close fit of these points with the experimental curve in Fig. 2 supports the view that when concentrated ammonia solution is used to prepare infusible white precipitate some fusible white precipitate ($HgCl_2,2NH_3$) may also be formed. For the corresponding bromides, Broderson and Rüdorff (*loc. cit.*) report that they have obtained mixed crystals of $NH_2 \cdot HgBr$ and $HgBr_2,2NH_3$ in the presence of traces of ammonium bromide. However, it is not possible to distinguish between $HgCl_2,2NH_3$ and the basic $x$HgO,$(1 - x)HgCl_2,2NH_3$ since they would give very similar nuclear resonance signals. Therefore $x$HgO,$(1 - x)HgCl_2,2NH_3$ could equally well be the impurity in sample B.

*Infusible White Precipitate, Sample C.*—The absorption curve is closely similar to that of A, Fig. 1. The dots on the absorption curve in Fig. 3 are the points calculated for pairs of protons 1·688 Å apart as done for sample A. It shows the central minimum very clearly, and there can therefore be very little hydrogen-containing impurity present. Quite small amounts of proton-containing impurity in which the protons occur in any arrangement except in relatively isolated pairs, are sufficient to mask the central minimum in the absorption curve. For example, if enamelled wire coils are used, the proton resonance signal of the very small amount of enamel present is sufficient to prevent the minimum in the absorption spectrum of infusible white precipitate from being observed. The presence of mercuric chloride impurity would have no effect on the proton resonance spectrum but, in view of the well-formed crystals of sample C obtained, and of the fact that the compound was recrystallised from concentrated ammonia solution, it is unlikely that much mercuric chloride can be present.

*Fusible White Precipitate.*—*X*-Ray measurements (Lipscomb, *Analyt. Chem.*, 1953, **25**, 737; MacGillavry and Bijvoet, *Z. Krist.*, 1936, **94**, 231) have been interpreted in terms of a cubic lattice of linear $(NH_3\text{–}Hg\text{–}NH_3)^{++}$ ions and chloride ions, the mercury ammine ions being aligned randomly along the crystal axes. A rigid structure of this type would be expected to give a proton resonance spectrum of the shape of Fig. 5*c*, and a second moment of about 36 gauss$^2$.

The experimental curve at 90° K shows only a single maximum and has a second moment of $10{\cdot}2 \pm 0{\cdot}7$ gauss$^2$. If the $NH_3$ groups were undergoing rotational reorientation about the Hg–N axis frequently enough, a line very similar to the experimental one would be expected, and its second moment would be about $\frac{1}{4}$ of 36 gauss$^2$, *i.e.*, $\sim$9 gauss$^2$. The circles in Fig. 4 represent the points calculated (Andrew and Bersohn, *J. Chem. Phys.*, 1950, **18**, 159) theoretically for an equilateral triangle of protons 1·682 Å apart, rotating about an axis perpendicular to their plane, and broadened by a gaussian function of second moment 3·5 gauss$^2$.

The proton resonance spectrum at 20° K is still partially narrowed, and its shape and width suggest that 20° K is within the range of the line-width transition from the narrowed line to the spectrum characteristic of the " rigid " structure.

This freedom of motion probably occurs because the $NH_3$ groups are in a very open lattice and spaced well away from the chloride ions. Similar effects have been observed with dimethylmercury (Gutowsky and Pake, *J. Chem. Phys.*, 1950, **18**, 162). The greater rigidity of the $NH_2$ groups in infusible white precipitate is probably associated with the long chains present in which the nitrogen atoms are linked each to two mercury atoms ($\text{–Hg–}\overset{+}{N}H_2\text{–Hg–}\overset{+}{N}H_2\text{–}$, etc.) (Lispcomb, *Analyt. Chem.*, 1953, **25**, 737).

In conclusion, it has been shown that the proton resonance spectrum of infusible white precipitate is consistent with the structure $NH_2{\cdot}HgCl$. The structures $NHg_2Cl,NH_4Cl$ and $x$HgO,$(1 - x)HgCl_2,2NH_3$ are excluded by the proton resonance spectra, at least for the samples studied. It seems likely that preparations of infusible white precipitate are often contaminated with mercuric chloride or with fusible white precipitate or its basic form depending upon the precise conditions of preparation. These conclusions are closely parallel to those of Broderson and Rüdorff, on the corresponding compounds formed from mercuric bromide and ammonia.

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