Quinine concentration being held constant, an increase in sulfuric acid concentration from 0.004 to 4 moles per liter shifts the whole absorption curve 200 cm.$^{-1}$ toward the red.

The ten-degree temperature coefficient, 1.12, agrees with one mode of calculating the temperature coefficient of the collision number in solution of a bimolecular reaction between activated quinine and H_2CrO_4 without additional energy of activation. Another calculation predicts a small energy of activation.

Ammines of the Lower Chlorides of Titanium

BY WALTER C. SCHUMB AND RICHARD F. SUNDSTRÖM

Although anhydrous titanium dichloride and trichloride have been the subject of numerous investigations, conflicting statements relative to some of their properties, and the absence of data concerning others, make the further study of these compounds desirable. In particular, the recorded observations which concern the preparation of the two chlorides appear in some respects to be in need of revision, and comparatively little is known concerning the reactions of these two substances with ammonia. The aim of the present paper is to contribute further information on each of these subjects.

Ruff and Neumann[1] prepared the anhydrous trichloride by reducing the tetrachloride with various metals. They obtained it as violet crystals, which when heated in a vacuum slowly began to sublime at 425°, and to decompose at 450° into the di- and tetrachlorides. At 475° this decomposition proceeded rapidly, and the dichloride thus obtained was very stable to heat and not volatile in a vacuum even at 600°. It is interesting to note that they were unable to obtain samples of high purity; they accounted for their high titanium content and low chlorine content by assuming that their samples had become oxidized during the course of the preparation. Earlier investigators similarly had failed to obtain pure specimens.

Meyer and co-workers[2] prepared the trichloride by the reduction of the tetrachloride with hydrogen at high temperatures, employing the hot-cold tube previously used by Georges and Stähler.[3] At 800–1000° they obtained a mixture of the di- and trichlorides, which was converted completely into the trichloride by heating to 300° in a stream of hydrogen and

(1) Ruff and Neumann, Z. anorg. allgem. Chem., 128, 81 (1923).
(2) Meyer, Bauer and Schmidt, Ber., 56, 1908 (1923).
(3) Georges and Stähler, ibid., 42, 3200 (1909).

tetrachloride vapor. Their final product, which had the appearance of violet scales, represented a yield of approximately 30%. To account for the large proportion of dichloride in the primary product, they assumed that the reduction to trichloride was not a simple one, but rather one involving two steps

$$TiCl_4 + H_2 = TiCl_2 + 2HCl \qquad (1)$$
$$TiCl_2 + TiCl_4 = 2TiCl_3 \qquad (2)$$
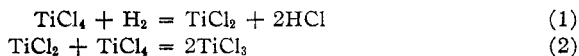
The first reaction supposedly took place in the hotter parts of the reaction tube and the latter in the colder. This assumption evidently presupposes that the dichloride is volatile at high temperatures, as indeed the earlier investigators claimed. Thus Friedel and Guérin[4] reported that the dichloride volatilizes at red heat and Stähler and Bachran[5] stated that the substance sublimes at 300° *in vacuo*. In view of the fact that, according to Ruff and Neumann, the trichloride sublimes at 425°, and then but slowly, the above statements appear doubtful, since in a series of chlorides volatility, in general, decreases with decreasing chlorine content.

Experimental

Preparation of Titanium Trichloride and Titanium Dichloride.—The titanium trichloride used in this work was prepared by reduction of the tetrachloride with hydrogen at 650°. The tetrachloride previously had been distilled several times in an atmosphere of dry carbon dioxide, the colorless fraction, b. p. 136–137°, being collected in sealed tubes each containing approximately 30 g. In the reduction a modified form of the hot-cold tube described by Young and Schumb was employed.[6] In order to minimize the danger of hydrolysis during the transfer of the tetrachloride from its sealed container to the apparatus, the substance was frozen and admitted against a brisk countercurrent of dry carbon dioxide into a flask which formed part of the apparatus; thence it was slowly distilled into a second flask and the former sealed off from the latter. A stream of dry, oxygen-free hydrogen, bubbling through the liquid, carried the tetrachloride vapor into the reaction chamber (35 cm. long and 30 mm. wide), which was heated in a hinged type electric furnace. The titanium trichloride formed was collected upon an 8-mm. tube, cooled internally by a rapid stream of water. The unchanged tetrachloride was recovered practically quantitatively from the effluent gas by passage through two traps, chilled to −20 and −78°, respectively.

Due to the reversibility of the reaction, $2TiCl_4 + H_2 \rightleftharpoons 2TiCl_3 + 2HCl$, in order to obtain satisfactory yields of the trichloride it is essential to remove the hydrogen chloride rapidly. Meyer and co-workers,[2] employing a gas mixture containing 16.6 mole per cent. of tetrachloride, and a reaction rate such that 20 to 30 g. of trichloride was formed in from three to four hours, accomplished this with the aid of metallic titanium present in the reaction tube. However, if a slower reaction rate was used together with a rapid hydrogen current, the concentration of hydrogen chloride could be kept low throughout the process. To this end a comparatively low reaction temperature should be used; this has the added advantage of permitting but slight decomposition of the trichloride formed. The gas mixture in the reaction chamber, moreover, should contain relatively little tetrachloride vapor; hence the liquid through which the hydrogen bubbles should be kept at a moderately low temperature. For this purpose the

(4) Friedel and Guérin, *Compt. rend.*, **81**, 889 (1875).

(5) Stähler and Bachran, *Ber.*, **44**, 2906 (1911).

(6) Young with Schumb, THIS JOURNAL, **52**, 4233 (1930).

vapor pressure of the tetrachloride at 25° was determined and found to be approximately 21 mm. From this it may be estimated that the mixture resulting from the passage of hydrogen through the liquid at 25° contained about 2.75 mole per cent. of tetrachloride vapor. The rate of flow 250 cc. of hydrogen per minute was adopted as the most suitable; under these conditions 30 g. of tetrachloride was volatilized in about nine hours. To ensure adequate drying of the gas at this rate of flow, four 60-cm. drying tubes, the first two containing "Dehydrite," the latter two phosphorus pentoxide, were used. Since the gas mixture rapidly passed through the reaction tube, a long hot space was desirable, and the cold tube accordingly was allowed to extend only 6 or 7 cm. into the heated zone, the resulting area of cooling surface being quite sufficient to collect the product.

The temperature of the reaction tube was raised gradually and at 600° a black deposit appeared on the tip of the cold tube. As the temperature approached 650° this deposit assumed a distinctly crystalline appearance, the crystals consisting of large thin plates as well as short needles, both *black* in color. When two or three grams of trichloride had collected on the cold tube the temperature was lowered to 300°, the stream of cold water shut off and the hydrogen current reduced to two bubbles per second. The flask containing the tetrachloride was warmed so as to allow these vapors to pass through in large quantities, in order that any dichloride present might thus be converted into the trichloride. When all the tetrachloride had vaporized, the slow hydrogen current was continued in order to remove any tetrachloride adhering to the trichloride or to the walls of the apparatus. The reaction chamber was then allowed to cool to room temperature and the hydrogen was displaced by dry, oxygen-free carbon dioxide. The traps containing the unchanged tetrachloride were then sealed off and by suitably rotating the reaction tube the black product was shaken down into a side tube, wherein it could be divided into two samples (each weighing about a gram) and sealed off.

The violet color hitherto ascribed to titanium trichloride is probably due to traces of moisture; when a sealed tube containing the black crystals is opened the color instantly changes to violet, although moist air has no apparent further effect for some time. The needles gave indications of being, in general, somewhat more reactive than the plates.

The action of heat on the trichloride was studied in a vacuum of approximately 0.001 mm. The temperature was raised slowly, and at 425–440° the crystals were observed to volatilize very gradually, thin transparent violet plates 3 or 4 mm. in diameter depositing just beyond the heated portion of the tube. The violet color in transmitted light is here due doubtless to the excessive thinness of the plates. At a slightly higher temperature, approximately 450°, the trichloride was observed to decompose, yielding the di- and tetrachlorides, the latter collecting as a white solid in the far end of the tube, which was chilled to −78°. While at 450° the decomposition was very slow, it proceeded at 475° at such a rate that a 1-g. sample required twelve hours for complete decomposition.

Attempts to prepare a dichloride of high purity failed, despite all precautions to exclude air and moisture. The purest sample obtained gave the following analysis: Ti, 41.5%; Cl, 56.4%; as compared with the calculated values, 40.4 and 59.6%, respectively. When the samples were treated with water, a small fraction, which proved to be elementary titanium, invariably remained unaffected. In order to determine whether this titanium was derived from decomposed dichloride, a specimen of the latter was introduced into one end of an evacuated tube and heated to 475°, the other end being chilled strongly. The appearance within a few hours of a white solid in the chilled end of the tube indicated that the reaction $2TiCl_2 = TiCl_4 + Ti$ had commenced. The volatility of the dichloride was next tested by heating in a vacuum over the range 300–600°, but at no time was any evidence of sublimation observed. The same experiment

was repeated in an atmosphere of hydrogen, but the appearance of tetrachloride constituted the only noticeable change.   The possibility that the dichloride is appreciably volatile *in vacuo* or in an atmosphere of hydrogen may therefore be excluded, and the hypothesis advanced by Meyer as to the mechanism of the reduction of the tetrachloride cannot be substantiated.   The large amount of dichloride obtained was probably due to the decomposition of the trichloride at the high temperature employed.

Since the dichloride is slowly decomposed at 475°, it is hardly possible to prepare it in a state of purity by the method above described.   Calculated on the basis of chlorine discrepancy, the decomposition of the dichloride we obtained amounts to approximately 5% of the original sample.   From the results of Ruff and Neumann the figures 8.4 and 9.2% are obtained, while the titanium content of Stähler and Bachran's dichloride ranged from 7.0 to 9.4%.

Reactions of Titanium Trichloride and Titanium Dichloride with Ammonia.— Georges and Stähler[3] reported that when titanium trichloride is shaken with liquid ammonia a yellow emulsion is formed, and part of the substance appears to dissolve, and Friedel and Guérin[7] studied the reaction between the dichloride and ammonia at red heat.   In view of the fact that these substances are extremely reactive toward water, it is reasonable to suppose that they should react with ammonia at low temperatures.

In some preliminary experiments ammonia was conducted over the two chlorides at room temperature; both swelled up considerably and heat was evolved.   The product formed was white in the case of the trichloride, but the dichloride yielded a pearl-gray substance.   The experiments were repeated at −78° and the same results were noted.   Two alternative modes of reaction are possible.   The two chlorides may form molecular addition compounds, as is generally the case with halides of the metallic elements; or, as frequently happens with halides of non-metallic elements, mixtures of ammonium chloride and an amide or imide of the non-metal (depending on the temperature) may be formed.   Stähler and Wirthwein[8] have reported the formation of titanic tetramide by the interaction of the tetrachloride with liquid ammonia.   With titanium in its *lower* valences it is of interest to determine whether, accompanying the increase in basigenic character of the element, the formation of true ammines becomes possible. The following experimental work, undertaken from this point of view, proves such to be the case.

Reaction of Titanium Trichloride with Ammonia.—The apparatus used was a modification of that which Thomas and Pugh[9] recently have employed in similar work on germanium tetrachloride.   This apparatus allowed ammonia to act on the chlorides at any temperature between −78° and room temperature, and also permitted the product formed to be thoroughly stirred and washed several times in liquid ammonia, so that any ammonium chloride might be removed.   In order to be sufficiently dried, the entire apparatus was alternately thoroughly evacuated and filled with dry carbon dioxide. This gas was taken from a ten-liter reservoir, which was equipped with a manometer and filled from a cylinder after passage of the gas through a purifying train to remove oxygen and moisture.   The trichloride was introduced from one of its sealed containers by opening one end and rapidly attaching it to a piece of heavy-walled rubber tubing, the other end of which was connected to the open tube (a), shown in the accompanying figure. The system was evacuated and refilled with carbon dioxide.   The trichloride was shaken down into the 26-mm. reaction tube (b) and the tube (a) sealed off as indicated.   The major portion of the crystals was caught in the shallow, heavily gold-plated copper dish (c).   This dish, about two mm. less in diameter than the reaction tube, was held in place

(7) Friedel and Guérin, *Ann. chim. phys.*, [5] **8**, 24 (1876).

(8) Stähler and Wirthwein, *Ber.*, **38**, 2619 (1905).

(9) Thomas and Pugh, *J. Chem. Soc.*, 61 (1931).

by indentations in the glass above and below, but was free to move vertically about two mm. The reaction tube was surrounded by a cylindrical vacuum jacket closed at the lower end with a rubber stopper. Connection between the receiver (d) and the reaction tube was at first made through a wide-bore stopcock, but this proved unsatisfactory, as when liquid ammonia filled the tube fissures formed in the lubricant, causing leakage of air. The connection was subsequently made with a thick-walled rubber tube, closed with the screw-clamp (g). The ammonia was conveyed from a cylinder into an evacuated bulb (e), where it was condensed and dried with sodium. Approximately one quarter of the liquid was then evaporated, the vapor, sweeping out any air and hydrogen, escaping through the mercury trap (f), which was arranged to serve as a manometer as well.

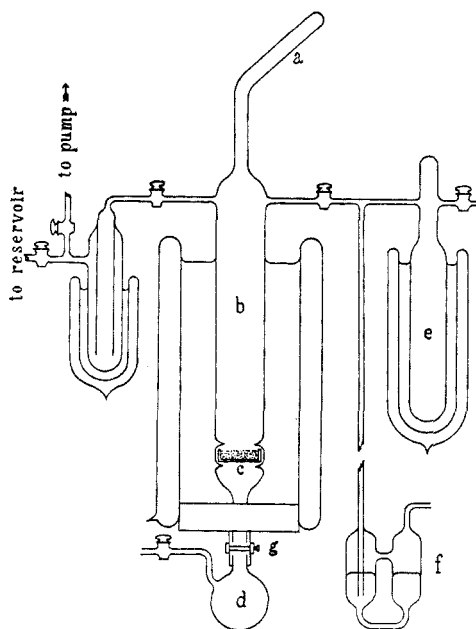The cylindrical vacuum jacket surrounding the reaction tube was cooled to −78°, the system evacuated with the screw-clamp (g) closed, and ammonia slowly admitted from (e). The trichloride swelled up to form a spongy mass, six or seven times its original volume, with but slight change in color. Ammonia was allowed to condense until the liquid entirely surrounded the spongy mass, which gradually collapsed to form a grayish powder. The supernatant liquid had a yellow color, as Georges and Stähler reported, but it was less pronounced after the second treatment and finally disappeared altogether. As the liquid was allowed to warm violent bumping commenced, and the vibrations of the dish caused the powder to be thrown about in it. This provided a means of thorough stirring; as the temperature was lowered the bumping ceased, and as the powder settled all but a small portion was caught in the dish. After this stirring process had been repeated a few times and the pressure of the ammonia had become atmospheric, the screw-clamp (g) was opened and the liquid passed down into (d), where it was allowed to evaporate. The clamp was closed, the reaction chamber again filled with liquid ammonia, and the above operations were repeated four or five times. The total time of exposure to ammonia was in no case less than twelve hours. If a mixture of imide and ammonium chloride had been formed, there was thus ample time and opportunity for the latter to be leached out by the liquid. After the last treatment the reaction tube was allowed to warm up to room temperature, the ammonia escaping through the mercury trap. In the first few experiments the ammonia was replaced by carbon dioxide; both gases were sufficiently dry to prevent any observable reaction between them. When the apparatus was completely filled with the latter gas, it was turned to a horizontal position and the product divided into two samples, which, one at a time, were shaken down into (a) and sealed off.

The product thus obtained is white, though grayish when moistened with liquid ammonia, and reacts violently with water—more so, in fact, than is the case with the

Fig. 1.

trichloride itself. When kept in a sealed tube in an atmosphere of carbon dioxide it darkens perceptibly within a day or two; hence it was preserved in an atmosphere of ammonia, even though this introduced complications in the subsequent analysis.

Analysis.—The sample was dissolved in dilute nitric acid and then boiled with an excess of alkali, the ammonia being collected in a known amount of acid. The apparatus consisted of a three-necked Woulfe bottle, through one neck of which the sample was introduced, while through a second neck alkali was admitted from a separatory funnel. The liberated ammonia was conveyed through a splash bulb and a condenser into an Erlenmeyer flask containing the acid, the excess of which was then determined by titration, using methyl red as indicator. This method was shown to yield sufficiently accurate results by separate experiments with known weights of pure ammonium chloride.

The sealed glass tube containing the sample to be analyzed, together with some free ammonia, was weighed and opened, correction being made for the buoyancy of the gas.[10] The open end was rapidly inserted into one neck of the thoroughly dried Woulfe bottle, while a counter current of dry air through the apparatus swept out the same neck. The free ammonia, lighter than air, was thus rapidly swept out in a few minutes by the air current. The neck was then closed by a rubber stopper and 2 N nitric acid slowly admitted from the funnel until a clear solution was obtained. Sodium hydroxide solution was added in considerable excess and water to make the volume 200 cc. The liquid was carefully boiled until its volume had been reduced to 50 cc., this operation requiring about two hours. The excess acid was then titrated with carbonate-free sodium hydroxide.

The liquid remaining in the Woulfe bottle was diluted and acidified with nitric acid. A precipitate containing titanium hydroxide and silicic acid (derived from the glass) appeared. This was filtered off, silver nitrate was added, and the chlorine determined in the usual manner. Titanium was not determined in the above-mentioned precipitate, but separate samples were dissolved in dilute nitric acid, the titanium precipitated with ammonia, washed, dried, ignited and weighed as TiO_2. The chlorine was also determined in these samples (I and II, below). The results agree reasonably well with the values calculated for titanium trichloride hexammine.

	I	II	III	IV	Calcd. for $TiCl_3 \cdot 6NH_3$
Ti	18.8$_2$	18.5$_9$	. . .	. . .	18.69
Cl	40.9$_4$	41.17	41.1$_1$	41.6$_6$	41.50
NH$_3$	. . .	. . .	39.7$_4$	39.5$_8$	39.81

Properties.—Titanium trichloride hexammine is a white powder which reacts violently with water, yielding the familiar solution of trivalent titanium. It dissolves in dilute nitric acid to form a clear solution. When exposed to air it smells strongly of ammonia and darkens rapidly. In a sealed tube filled with dry carbon dioxide it darkens less rapidly, but nevertheless appreciably.[11] It decomposes even when preserved in contact with dry ammonia at atmospheric pressure. Thus after a week a 0.8332-g. sample so preserved contained only 36.6% of ammonia. When gently heated in a vacuum it readily gives up four moles of ammonia and turns black, but the remaining two moles appear to be held tenaciously. The

(10) As the tubes were never more than 12 cc. in volume, they contained less than 0.01 g. of free ammonia.

(11) After five days a 0.5037-g. sample kept in a 12-cc. tube showed but 32.4% NH$_3$.

resulting black substance is so reactive that it catches fire on exposure to moist air.

The thermal decomposition of the hexammine was studied quantitatively. The ammonia set free by heating the substance in a Wood's metal bath at 300° was condensed in a bulb immersed in liquid air. When the decomposition appeared to be complete, as indicated by the color of the residue and by the fact that no further ammonia condensed, the bulb was sealed off and the weights of the black residue and ammonia were determined. The percentages of ammonia released from the original samples correspond to 4.08 and 4.15 moles, respectively.

	Wt. residue	Wt. NH$_3$	% NH$_3$ evolved from orig. sample
I	0.4743	0.1760	27.07
II	1.2390	.4722	27.53

The black residue was then analyzed for titanium and chlorine in the usual manner, but the content of ammonia, though its presence was shown qualitatively, was determined by difference. This difference was calculated on the assumption that the original material before heating contained 39.81% of ammonia. From this amount the weight of ammonia condensed by the liquid air was deducted, after the necessary corrections for the presence of free ammonia in the sample tube had been made.

	I	II	Calcd. for TiCl$_3$·2NH$_3$
Ti	26.1	26.4	25.5
Cl	55.7	56.0	56.4
NH$_3$	17.5	16.9	18.1

Although the evidence offered by the preceding analyses is not considered sufficient to afford conclusive proof of the existence of a diammine of titanium trichloride, it indicates that on gentle heating the hexammine gives off four moles of ammonia, and the resulting substance is probably a diammine and not a chloronitride, such as Ruff and Eisner reported in the case of the decomposition of the tetrachloride hexammine.[12] As the temperature is raised, no more ammonia is set free, and finally a second decomposition occurs, involving the disintegration of the trichloride. Ammonium chloride was identified as one of the products.

Reaction of Titanium Dichloride with Ammonia.—The apparatus and procedure employed was the same as that used with the trichloride. The dichloride was in contact with liquid ammonia for a period of twelve hours, during which time the material was thoroughly stirred and washed five or six times. Because the dichloride is a fine dry powder, as compared with the comparatively large crystals of the trichloride, a larger amount was lost during the stirring operations, and therefore the samples were rather small.

(12) Ruff and Eisner, *Ber.*, **41**, 2250 (1908).

In other respects the dichloride behaved as did the trichloride; the product, however, was pearl gray rather than white.

Analysis.—The method of analysis for ammonia and chlorine was that used with the corresponding compound of the trichloride. A Pyrex Woulfe bottle, which was found to be resistant to the action of a boiling alkali solution, was employed, and the amount of silica dissolved was sufficiently small to allow the determination of titanium in the same sample. Before the final weighing of titanium dioxide, any silica that might possibly be present was volatilized by heating with hydrofluoric and sulfuric acids.

Due to the difficulty of obtaining specimens of titanium dichloride free from both the trichloride and elementary titanium, the samples of reaction product were never wholly pure. Inasmuch as elementary titanium does not react with ammonia under the conditions used, it was thought less objectionable to work with samples containing 5% of free titanium, rather than with samples containing small amounts of trichloride. When samples of the reaction product were treated with water a small fraction remained unaffected, as with the dichloride itself, but as the solution above was always turbid from hydrolysis, it was not feasible to separate the free titanium by filtration. The content of elementary titanium in the samples was determined by independent analysis of the original dichloride, and also by noting the amount of titanium in the reaction product in excess of the atomic ratio 1:2. Both methods gave approximately the same results, the composition of the product corresponding reasonably well with the formula $TiCl_2 \cdot 4NH_3$.

	I	II	III	Calcd. for $TiCl_2 \cdot 4NH_3$
Ti	25.2$_6$	25.1$_0$	25.7$_3$	25.63
Cl	37.2$_6$	37.1$_4$	37.3$_4$	37.92
NH_3	35.8$_3$	36.6$_1$	36.1$_3$	36.45

Properties.—Titanium dichloride tetrammine as thus obtained is a pearl-gray powder which smells strongly of ammonia when exposed to air. It dissolves in water with the evolution of hydrogen, yielding a dark brown, turbid solution, but the reaction is slower than that of the dichloride itself. Dilute nitric acid dissolves it with a hissing sound, forming a yellow solution which is not quite clear, and as in the case of the water solution minute particles of elementary titanium remain undissolved. When heated at 300° in a vacuum it gives off ammonia, ammonium chloride appearing simultaneously. This was driven to the cooler parts of the tube, and when the decomposition appeared to be complete the black residue was sealed off and analyzed. It was found to contain approximately 60% of titanium, and is presumably a nitride; a sample free from chlorine was never obtained, five or six per cent. of the latter invariably remaining despite continued heating. The presence of nitrogen was shown qualitatively, but

specimens sufficiently pure to justify a quantitative analysis could not be obtained.

The authors are indebted to Dr. E. Lee Gamble for kind assistance in some of the analytical work.

Summary

Anhydrous titanium trichloride, prepared by the reduction of the tetrachloride with hydrogen at 650°, exists in two crystal forms, plates and needles, both *black* in color in reflected light. Exceedingly thin plates show a violet color in transmitted light. The data of Ruff and Neumann relating to the behavior of the trichloride when heated in a vacuum are confirmed.

Anhydrous titanium dichloride, prepared by the thermal decomposition of the trichloride, is slowly decomposed when heated in a vacuum to 475°. Therefore specimens of the dichloride so prepared are inevitably contaminated with free titanium. No evidence of volatility is obtained when the dichloride is heated over the range 300–600°, either in a vacuum or in an atmosphere of hydrogen. The hypothesis concerning the mechanism of reduction of the tetrachloride by hydrogen, advanced by Meyer, Bauer and Schmidt, therefore cannot be substantiated.

The trichloride combines with ammonia at low temperatures to form a white hexammine. Liquid ammonia does not dissolve out any ammonium chloride, despite prolonged stirring and washing. The possibility that the compound is not a true ammine, but rather a mixture of an imide and ammonium chloride, is therefore excluded. On heating to 300° the hexammine readily gives off four moles of ammonia, a reactive, black substance, probably a diammine, remaining behind.

The dichloride likewise reacts with ammonia at low temperatures, yielding a pearl-gray tetrammine, the properties of which are in general similar to those of the hexammine of the trichloride.