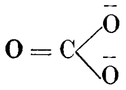
CCCXCII.—*Studies in Complex Salts. Part I. The Preparation and Properties of Some Selenitopentamminecobalt Salts.*

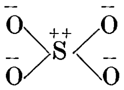
By Harry Lister Riley.

Although carbonatopentammine compounds have been described (Werner and Goslings, *Ber.*, 1903, **36**, 2378), the carbonate ion appears to have a greater tendency to occupy two positions in the complex, as judged from a consideration of methods of preparation and relative yields. Complex salts have been described containing sulphato-, sulphito- (Riesenfeld, *Z. anorg. Chem.*, 1924, **132**, 99), chromato- (Briggs, J., 1919, **115**, 67), and selenato- (Meyer, *Z. anorg. Chem.*, 1921, **118**, 1) groups, and in the case of the first three groups both pentammine and tetrammine compounds have been prepared. Riesenfeld pointed out (*loc. cit.*) that the sulphito-group almost invariably occupies only one position in the co-ordination complex, and advanced experimental evidence in favour of a tetrahedral structure for those compounds where this group has been represented as occupying two positions in the complex. The tetrammine sulphato- and chromato-compounds were prepared from the corresponding carbonato- or diaquo-tetrammine compound, and there is no record of these compounds having been prepared in a manner similar to that employed in the case of the carbonatotetrammine compound (Jörgensen, *Z. anorg. Chem.*, 1892, **2**, 282).

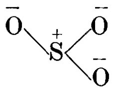
The reason for this difference in the properties of these ions becomes apparent on the basis of modern electronic theory. The tendency of a molecule or ion to enter the co-ordinated complex depends on its possession of a " lone pair " of electrons and upon the distribution of the charges within the molecule or ion. A comparison of the structure of the various ions under consideration at once suggests an explanation of their differences in behaviour.



Carbonato-.
Co-ordinate valency
usually 2.



Sulphato-.



Sulphito-.

Co-ordinate valencies
usually 1.

The effect of the positive charges on the sulphur atom is to cause the electrons round the oxygen atoms to be held much more firmly and to reduce their tendency to form a co-ordinate link. When one link is formed, the tendency to form a second will be less still. In the carbonato-ion the carbon atom is electrically neutral, so the negative oxygen atoms will possess a greater tendency to form a co-ordinate link than if the carbon atom were positively charged. The formation of one co-ordinate link will reduce the tendency to form a second.

In order to test the above ideas, it was decided to attempt the preparation of some selenito-complex salts (which have not previously been described) by a method similar to that employed in the preparation of carbonato-tetrammine and -pentammine compounds, examining the product of oxidation for both pentammine and tetrammine compounds.

EXPERIMENTAL.

Preparation of Selenitopentamminecobaltic Chloride.—To 18 g. of freshly precipitated cobaltous hydroxide were added 22 g. of selenium dioxide (prepared from metallic selenium by oxidation with nitric acid and subsequent sublimation), and 11 g. of ammonium chloride, followed by a little water and a large excess of ammonia (*d* 0·880). The whole was well stirred until everything soluble had dissolved. A rapid current of air was passed through the filtered solution until it no longer contained free ammonia (about 12 hrs.), its colour changing from brownish-red to a deep ruby-red. The solution (about 400 c.c.) was evaporated to 100 c.c. in a vacuum over concentrated sulphuric acid. As no crystallisation had occurred at this stage, 250 c.c. of alcohol were slowly added with continuous stirring. A deep red, oily liquid separated which slowly solidified to a crystalline mass. The clear supernatant liquid was decanted, and on being tested with barium chloride showed the presence of selenite ions. The solid mass was dissolved in 100 c.c. of water and again precipitated with 250 c.c. of alcohol. The supernatant liquid, which was again decanted, gave no precipitate with barium chloride. The solid was dissolved in 80 c.c. of water, 150 c.c. of alcohol were added, and the mixture was kept for 2 days, a few c.c. of alcohol being added from time to time. It was thus possible to grow quite large crystals, some of them about 2 cm. long, which on examination under the microscope, proved to be not single crystals but aggregates of small crystals belonging to either the rhombic or the tetragonal system. The large crystals were deep brownish-red, whereas the small, rapidly precipitated crystals were much lighter in colour. A yield of over 80% of *selenitopentamminecobaltic chloride* (of above 98% purity) was obtained (Found : Co, 19·36; SeO_3, 40·81; NH_3, 27·34; Cl, 11·72; Co : SeO_3 : NH_3 : Cl = 1·02 : 1·00 : 5·01 : 1·03. $[Co(SeO_3)(NH_3)_5]Cl$ requires Co, 19·22; SeO_3, 41·49; NH_3, 27·72; Cl, 11·57%). Some of the crystals, after being air-dried, were placed in a vacuum desiccator over sulphuric acid for 2 days. No loss in weight occurred.

Analysis.—The following method was adopted for the analysis of the crystals. *Selenium.* About 0·3 g. of the substance was dissolved in 100 c.c. of water, 2—3 c.c. of concentrated hydrochloric acid were added, and then 30 c.c. of saturated sulphurous acid solution, and the whole was boiled for 5 hours, with the addition of more sulphurous acid from time to time. The precipitated selenium was washed, dried at 90—95°, and weighed.

Cobalt. The filtrate from the selenium was evaporated to dryness with the addition of a slight excess of sulphuric acid. The cobalt sulphate formed was heated at 400—450° and weighed. Ammonia and chlorine were estimated by the usual methods.

The reactions of the compound proved conclusively that it possessed the assigned constitution. Its solution in water, in which it is extremely soluble, gives no precipitate with barium chloride in the cold, showing the absence of selenite ions. On boiling, a precipitate containing barium, cobalt, and selenium is thrown down. Sulphur dioxide precipitates selenium from a hot solution containing hydrochloric acid, but the precipitation is complete only after prolonged boiling (see analysis, above). A concentrated solution of the salt containing a little sulphuric acid gives a precipitate with ferrous sulphate solution only after a few minutes' boiling. Hydrogen sulphide gives an immediate precipitate of sulphur and selenium.

Silver nitrate precipitates the chlorine completely from a cold solution. Sodium hydroxide only precipitates the cobalt on boiling, ammonia being evolved. When a solution of the compound is boiled with dilute hydrochloric acid (1 : 3), a ruby-red, crystalline substance is precipitated; this was shown to be chloropentamminecobaltic chloride : $[Co(SeO_3)(NH_3)_5]Cl + 2HCl = [CoCl(NH_3)_5]Cl_2 + H_2SeO_3$. Molecular-weight determinations (cryoscopic in water) indicated that the compound is a binary electrolyte of the above formula, dissociating to the extent of 80% in $0{\cdot}23N$-solution and 97% in $0{\cdot}1N$-solution.

Another series of experiments was made in which various fractions, obtained by precipitating the original oxidised solution with alcohol, were analysed : in no case was the ratio $NH_3 : SeO_3$ less than 5 : 1. The high solubility of these selenito-compounds makes it impossible to be sure that no tetrammine compound is formed, but the above experiments prove that, if it is formed at all, it can only be present in very small amounts.

Selenitopentamminecobaltic Selenite.—An attempt to prepare this compound was made by the following method : To 18 g. of freshly precipitated cobaltous selenite were added 6 g. of selenium dioxide, a little water, and a large excess of ammonia (*d* 0·880). The resulting clear solution was oxidised by a rapid current of air until free from excess of ammonia (12 hrs.). The solution was evaporated in a vacuum over concentrated sulphuric acid. No crystallisation occurred, but a thick, oily syrup resulted. This was dissolved in a little water, and the filtered solution precipitated with alcohol, the process being carried out five times. The resulting syrup was evaporated in a vacuum over concentrated sulphuric acid for several days, and then solidified to a dark red, crystalline mass [Found : Co, 16·51; SeO_3, 52·75; NH_3, 23·28; H_2O (by diff.), 7·46. $[Co(SeO_3)(NH_3)_5]_2SeO_3,3H_2O$ requires Co, 16·29; SeO_3, 52·74; NH_3, 23·50; H_2O, 7·46%], which was extremely deliquescent, rapidly changing to a viscous liquid on exposure to the atmosphere. The aqueous solution rapidly became turbid. Barium chloride precipitated barium selenite along with some cobalt selenite from the cold solution. On removing this precipitate and reducing the acidified filtrate with hydroxylamine hydrochloride, selenium was precipitated, thus indicating the presence of both ionised and co-ordinated selenite groups. Water was shown to be present in the compound qualitatively; it was not removed by long exposure to sulphuric acid in a vacuum. The compound analysed was probably appreciably decomposed.

An attempt to estimate ionised and co-ordinated selenium separately led to inconclusive results. Hydrolysis always occurred during attempts to dissolve the substance even in ice-cold water. The analysis showed, however, that the substance does contain the selenito-group in the complex and that the ratio $NH_3 : SeO_3$ is 5 : 1·5, which is in agreement with the proposed formula. The high solubility and rather unstable nature of the substance make it impossible to obtain it pure.

Summary.

Ions which possess an electrovalency of two show varying co-ordination valencies. The carbonate ion usually occupies two positions, but sometimes only one. Ions of the sulphate and sulphite types possess a greater tendency to occupy one position in the complex. An explanation of this behaviour is advanced, and evidence in agreement with this explanation is obtained from a study of the properties of two selenitopentamminecobaltic salts which were specially prepared for this purpose.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.

[*Received, July* 17*th*, 1928.]