

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 17]

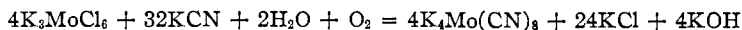
## A COMPLEX CYANIDE OF TRIVALENT MOLYBDENUM

BY RALPH C. YOUNG

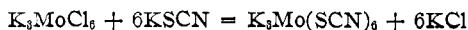
RECEIVED DECEMBER 7, 1931

PUBLISHED APRIL 6, 1932

Although complex chlorides, bromides and thiocyanates of trivalent molybdenum are known, previous attempts to produce a trivalent complex cyanide have resulted in the formation of the octacyanide of tetravalent molybdenum, and it has been the practice to consider the oxidation of the molybdenum as due to the oxygen of the air and to express the result by equations similar to the following



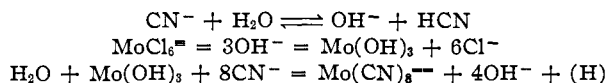
as was done by Bucknall and Wardlaw.<sup>1</sup> In the case of the thiocyanate, however, replacement occurs without oxidation



The problem of ascertaining why oxidation should take place in the case of the cyanide and not in that of the thiocyanate was undertaken with a view to applying the facts found to the prevention of this oxidation and the preparation of a trivalent complex cyanide.

The oxidation of the molybdenum to the tetravalent condition, it was found, could not be prevented when the reaction between potassium molybdenum hexachloride,  $K_3MoCl_6$ , prepared by the method of Bucknall, Carter and Wardlaw,<sup>2</sup> and potassium cyanide was carried out at approximately  $90^\circ$  in oxygen-free water and in an atmosphere of nitrogen, nor when the reaction was allowed to take place at the above temperature in a previously evacuated apparatus.

When potassium molybdenum hexachloride was heated with potassium hydroxide solution in the absence of air, the precipitated black sesquioxide was found to react with the water to evolve hydrogen, the molybdenum being oxidized to a higher valence state. It is known that the sesquioxide is oxidized in the air to the brown dioxide. Since potassium cyanide solution was found to react in presence of air with the sesquioxide and also with the dioxide to produce the octacyanide, it would seem possible that the following series of changes could take place at elevated temperatures in the absence of oxygen, in the reaction between the complex hexachloride and potassium cyanide solution.



<sup>1</sup> Bucknall and Wardlaw, *J. Chem. Soc.*, 2988 (1927).

<sup>2</sup> Bucknall, Carter and Wardlaw, *ibid.*, 512 (1927).

One noted the dark red solution, the color of which is due to the  $\text{MoCl}_6^{3-}$  ion, change to a black opaque colloidal solution and finally to a transparent orange-yellow due to the  $\text{Mo}(\text{CN})_6^{3-}$  ion. The black colloidal material is probably molybdenum trihydroxide, as one obtains the same result when the hexachloride is first treated with alkali. No hydrogen is evolved in the reaction of potassium molybdenum hexachloride with potassium cyanide, although it was formed with potassium hydroxide. The fact that hydrogen is not evolved may be accounted for on the assumption that it is consumed by interaction with hydrocyanic acid, which is known to be reduced by metals in acid solution to methylamine and in neutral solution to formaldehyde and ammonia.

**The Preparation of Tripotassium Molybdenum Heptacyanide Dihydrate.**—By allowing the reaction between potassium molybdenum hexachloride and potassium cyanide to take place at room temperature, in oxygen-free water, and in an atmosphere of nitrogen, there was obtained a black, crystalline compound of trivalent molybdenum, analyses of which correspond to the formula,  $\text{K}_4\text{Mo}(\text{CN})_7 \cdot 2\text{H}_2\text{O}$ , or  $\text{K}_4\left[\text{Mo}\left(\frac{\text{CN}}{\text{H}_2\text{O}}\right)_7\right] \cdot \text{H}_2\text{O}$ . The method of preparation follows.

Seven grams of the hexachloride and 12 g. of potassium cyanide were introduced into the reaction vessel at C, Fig. 1, while nitrogen was allowed to enter at A. Tube C was sealed near the end, the nitrogen escaping now at B. After all the air was displaced with nitrogen, 70 cc. of water saturated with nitrogen was allowed to enter at B by opening D, A being closed. Stopcocks D and B were now closed and the tube with contents was shaken until complete solution had taken place. The red transparent solution gradually assumed an opaque, black and colloidal appearance and finally at the end of eighteen hours was again transparent and of a red-brown color. Thirty cc. of alcohol saturated with nitrogen was allowed to enter the reaction vessel through tube B, and was thoroughly mixed with the contents. No precipitation took place but on cooling the vessel in ice water black crystals were deposited in the form of flat plates. They fell to the bottom of the container and after crystallization was complete, the supernatant liquid was allowed to run out at A while nitrogen passed in at B. The crystals were washed several times with 80% alcohol, saturated with nitrogen, and finally with 95% alcohol alone, care being taken to prevent the admission of air to the reaction vessel. The tube C was now broken and the black solid, covered with alcohol, removed to a tube where it was washed several times by decantation with alcohol and finally dried *in vacuo*. The black crystals were analyzed for potassium, molybdenum, cyanogen content and water. The potassium was obtained as potassium sulfate and the molybdenum as lead molybdate from separate solutions made by decomposing 0.25-g. samples of the compound with concentrated nitric acid, evaporating to dryness, and by subsequently dissolving the residue in water. The molybdenum was removed as barium molybdate in the procedure for the determination of the potassium. The cyanide content was determined by the method of Bellucci and

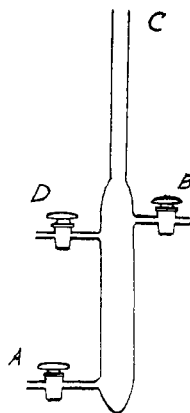


Fig. 1.—Apparatus for the preparation of  $\text{K}_4\text{Mo}(\text{CN})_7 \cdot 2\text{H}_2\text{O}$  in the presence of nitrogen.

Ricca.<sup>3</sup> The water was obtained by the heating of 1-g. samples in a current of dry oxygen at 300°, the moisture being collected in a weighed calcium chloride-Marchand tube.

The results of the above analyses were: K, 33.24, 33.29; Mo, 20.53, 20.30; CN, 38.52, 38.59; H<sub>2</sub>O, 7.60, 7.87. These results point to the formula, K<sub>4</sub>Mo(CN)<sub>7</sub>·2H<sub>2</sub>O, the theory for which requires: K, 33.24, Mo, 20.41; CN, 38.69; H<sub>2</sub>O, 7.66. It is likely that one or both molecules of water are in the complex giving the molybdenum a coordination number of eight.

As a test for the valency of the molybdenum, the procedure of Collenberg<sup>4</sup> was followed, who examined the octacyanide. A sample of the heptacyanide, weighing 0.3295 g., was oxidized with hot ferric alum solution in the presence of mercuric sulfate, the molybdenum being oxidized to the hexavalent condition. The ferrous salt formed was titrated with standard permanganate solution; 2.20 milliequivalents of permanganate were used, the theoretical for Mo<sup>+3</sup> → Mo<sup>+6</sup> being 2.10 milliequivalents and for Mo<sup>+4</sup> → Mo<sup>+6</sup>, 1.4 milliequivalents. Subsequent determinations checked these results and the conclusion must be drawn that the compound is one of trivalent molybdenum.

The coordination number of molybdenum is represented in this compound at eight as in the other cyanides of molybdenum of valence four and five, K<sub>4</sub>Mo(CN)<sub>8</sub>·2H<sub>2</sub>O and K<sub>2</sub>Mo(CN)<sub>8</sub>. Attempts to prepare a complex cyanide of trivalent molybdenum in which the molybdenum would have a coordination number of six, by the use of an amount of potassium cyanide smaller than that required for the complete reaction with the complex hexachloride, resulted in the same black heptacyanide.

Potassium molybdenum heptacyanide dihydrate gradually changes in moist air to the yellow octacyanide. It is very soluble in water, forming a brown solution which on great dilution becomes pink, the color one associates with other anions of complex molybdenum salts containing trivalent molybdenum. Potassium permanganate is reduced by the heptacyanide and the yellow color of the Mo(CN)<sub>8</sub><sup>3-</sup> ion first appears, only to be destroyed by further addition of permanganate. With alkalis black molybdenum trihydroxide is formed. Colored precipitates were obtained when solutions of the heptacyanide were treated with the following solutions, air being excluded in these tests: with lead acetate, red-brown; with zinc sulfate, gray; with manganese sulfate, grayish-green; with cobalt chloride, dark gray; with nickel chloride, green; with copper sulfate, dark purplish-brown; with ferrous sulfate, light blue.

Work is now in progress in this Laboratory on the corresponding complex cyanide of tungsten.

### Summary

By allowing K<sub>3</sub>MoCl<sub>6</sub> to react with potassium cyanide solution at room temperature and in the presence of nitrogen there is produced a complex cyanide of trivalent molybdenum, analyses of which correspond to a formula of  $\bar{K}_4\left[\text{Mo}\begin{matrix} \text{(CN)}_7 \\ \text{H}_2\text{O} \end{matrix}\right] \cdot \text{H}_2\text{O}$ , as does the quantitative examination of its reducing power.

The fact that potassium thiocyanate reacts in the presence of air with K<sub>3</sub>MoCl<sub>6</sub> solution to produce K<sub>3</sub>Mo(SCN)<sub>6</sub> while under like conditions potassium cyanide reacts to give K<sub>4</sub>Mo(CN)<sub>8</sub> is accounted for by assuming an intermediate formation of Mo(OH)<sub>3</sub>, due to the alkali formed by the hydrolysis of the cyanide. This hydroxide is readily oxidized in the air

<sup>3</sup> Bellucci and Ricca, *Atti congresso naz. chim. pura applicata*, 476 (1923).

<sup>4</sup> Collenberg, *Z. anorg. allgem. Chem.*, **121**, 310 (1922).

to the brown dioxide. Both the trivalent hydroxide and the dioxide are dissolved by long heating with a solution of potassium cyanide in contact with air, and give the octacyanide. The fact, too, that in the presence of nitrogen a solution of  $K_3MoCl_6$  and potassium cyanide react, when heated, to form  $K_4Mo(CN)_8$  was made clear after it was noted that  $K_3MoCl_6$  in alkaline solution, when heated in the absence of oxygen, reacts with the water, the molybdenum being oxidized and hydrogen being evolved.

CAMBRIDGE, MASSACHUSETTS

---

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR  
MEDICAL RESEARCH]

## AN EQUATION FOR ELECTROLYTIC CONDUCTANCE

BY THEODORE SHEDLOVSKY

RECEIVED DECEMBER 11, 1931

PUBLISHED APRIL 6, 1932

Debye and Hückel<sup>1</sup> have proposed a theory for the effect of the ionic atmosphere on the mobilities of ions. According to that theory the decrease in equivalent conductance should be proportional to the square root of the concentration, a relation which was first found empirically by Kohlrausch. The theoretical calculations for the decrease of ionic mobility with increasing concentration consider two effects. In the first place, when an ion moves through a solution under the influence of an applied electric field, it tends to disturb the surrounding ionic atmosphere, which then exerts an opposing electric force. In the second place, the ions comprising the ionic atmosphere produce a counter current of solvent which also retards the motion of the central ion.

However, Onsager<sup>2</sup> has pointed out that in calculating the first or so-called ionic effect, Debye and Hückel neglected to take into account the influence of the Brownian movement of the ions, and also used a treatment which is valid only if the negative and positive ions have equal mobilities. Furthermore, he has shown that the second or electrophoretic effect could be calculated in a manner which does not involve the ionic radii. Onsager's treatment likewise confirmed the square-root relationship between the equivalent conductance decrease and concentration, and, what is very important, the proportionality factor in his theoretical expression can be readily calculated from well-known constants.

Although Onsager's equation has been shown to be in close agreement with measurements at very low concentrations, it is strictly valid only as a limiting expression. This is so because in the derivation of the simple equation, only the first approximations were retained in the mathematical

<sup>1</sup> Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

<sup>2</sup> Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).