hexanitratocerate(IV). It is possible that other quadrivalent elements may have the same coördination number (6) in 12-heteropoly compounds. No X-ray studies appear to have been made with 12-heteropoly molybdo compounds of quadrivalent zirconium, thorium, germanium and tin, but salts with Miolati–Rosenheim formulas have been reported as

$(NH_4)_4H_4[Zr(Mo_2O_7)_6]\cdot 8H_2O$ $K_4H_4[Zr(Mo_2O_7)_6]\cdot 16H_2O$
$(CN_3H_6)_4H_4[Ge(Mo_2O_7)_6]$ $(NH_4)_8[Th(Mo_2O_7)_6]\cdot 15H_2O$
$(NH_4)_6H_2[Th(Mo_2O_7)_6]\cdot 11H_2O$ $Na_8[Th(Mo_2O_7)_6]\cdot 15H_2O$
$Na_6H_2[Th(Mo_2O_7)_6]\cdot 17H_2O$ $Ag_8[Th(Mo_2O_7)_6]$, $(NH_4)_8[Sn(Mo_2O_7)_6]\cdot 20H_2O$ and $(NH_4)_3H_5[Sn(Mo_2O_7)_6]\cdot 4H_2O$[15-18]

It seems probable that the coördination number is four in the zirconium and germanium compounds, and that they belong to the $H_{(8-n)}[XO_4Mo_{12}O_{36}]$ type. The thorium compounds, like those of cerium, appear to be derivatives of an octabasic acid, which may be formulated as $H_8[ThO_6Mo_{12}O_{36}]$. The case for the tin compounds is less clear and requires further study.

(15) G. A. Barbieri, *Atti Accad. Lincei*, [5] **28**, 781 (1913).
(16) C. G. Grossup, THIS JOURNAL, **52**, 5154 (1930).
(17) E. Pechard, *Compt. rend.*, **117**, 788 (1893).
(18) A. Rosenheim, *Z. anorg. Chem.*, **96**, 139 (1916).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

The Reduction of Potassium Hexacyanomanganate(III) by Potassium in Liquid Ammonia

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The reduction of potassium hexacyanomanganate(III) by potassium in liquid ammonia results in the formation of a yellow product which is difficultly soluble in liquid ammonia and possesses strong reducing properties. The properties of the product, as determined by four different methods—reacting ratio studies, chemical analysis, reducing power determination and magnetic measurements—show it to contain manganese in a state which can only be characterized as intermediate between the unipositive and the zero oxidation state. If the product is regarded as containing both of these forms of manganese, they must be present in at least approximately the atomic ratio of 1:1. Its composition may be represented by the formula $K_5Mn(CN)_6\cdot K_6Mn(CN)_6\cdot 2NH_3$.

There is excellent evidence that unipositive manganese may exist in the form of cyanomanganate[1] complexes. Manchot and Gall[1] have demonstrated that potassium or sodium hexacyanomanganate(II) is reduced in an alkaline medium in an atmosphere of hydrogen by aluminum powder to give a yellow solution possessing strong reducing power. From such solutions these investigators isolated white solids containing the hexacyanomanganate(I) ion, $[Mn(CN)_6]^{-5}$. The evidence[1b] reported for the existence of the tricyanomanganate(I) ion is less convincing. Electrolytic reduction of the hexacyanomanganate(II) ion at a platinum cathode gives a white product which appears to contain unipositive manganese.[2,3] There remains, however, some question regarding the exact nature of this substance. Fernelius and Hood[4] have studied the reduction of potassium hexacyanomanganate(III) by potassium in liquid ammonia and have proposed that the orange product formed is $K_5Mn(CN)_6\cdot NH_3$. The present communication is also concerned with the reduction of potassium hexacyanomanganate(III) by potassium in liquid ammonia and describes the preparation of a yellow substance containing manganese in both the unipositive and the zero oxidation state, the composition of which may be represented by the formula $K_5Mn(CN)_6\cdot K_6Mn(CN)_6\cdot 2NH_3$.

Experimental

Materials.—The liquid ammonia was taken directly from commercial cylinders of the synthetic material. The potassium, obtained from the Mine Safety Appliances Company, was used without further purification. Potassium hexacyanomanganate(III) was prepared according to the method of Lower and Fernelius[5] and purified in the following manner. The impure crystals were placed in a large fritted-glass filter of medium porosity which was attached to a filter flask containing absolute ethanol. Just sufficient water was added to dissolve the crystals, and the solution was drawn into the ethanol by means of an aspirator. Any oxide formed by hydrolysis remained on the filter. As the aqueous solution came in contact with the ethanol, dark red crystals of potassium hexacyanomanganate(III) were formed. Two additional precipitations from ethanol gave a product of practically the theoretical manganese content.

Apparatus and Reduction Procedure.—The apparatus employed in the reductions is illustrated in Fig. 1. Individual sections of the apparatus were connected by means of flexible Tygon tubing. The reaction chamber was about 3.5 cm. in diameter and approximately 25 cm. high. Duplicate sampling bulbs A and B were inserted in the reaction chamber through ground glass joints. The ammonia delivery tube extended close to the bottom of the reaction chamber in order that the ammonia which was bubbled through during the course of the reaction might have a stirring effect on the reaction mixture. The presence at C of a large standard taper joint permitted the removal of the lower part of the reaction chamber for sampling purposes. The fritted-glass disk sealed into the bottom of the reaction chamber served, after withdrawal of the solvent into the filter trap by means of an aspirator, to hold the insoluble product formed in the reduction reactions.

Prior to each reduction the several pieces of the reaction chamber assembly were cleaned and dried in an oven at 110°. The apparatus was then completely assembled except for the sampling bulbs. The openings for the bulbs were stoppered with standard taper plugs and ammonia was passed through the system for at least one hour to sweep out the air and to dry the apparatus. The sampling bulbs were charged with weighed quantities of the reactants (the molar ratio of potassium to manganese(III) complex always being greater than 2.5:1), flushed with ammonia, and quickly inserted into the reaction chamber, a positive internal pres-

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[1] (a) W. Manchot and H. Gall, *Ber.*, **60B**, 191 (1927); (b) **61B**, 1135 (1928).
[2] G. Grube and W. Brause, *ibid.*, **60B**, 2773 (1927).
[3] W. D. Treadwell, O. Gübeli and D. Huber, *Helv. Chim. Acta*, **24**, 152 (1941).
[4] W. C. Fernelius, private communication.
[5] J. A. Lower and W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 213.

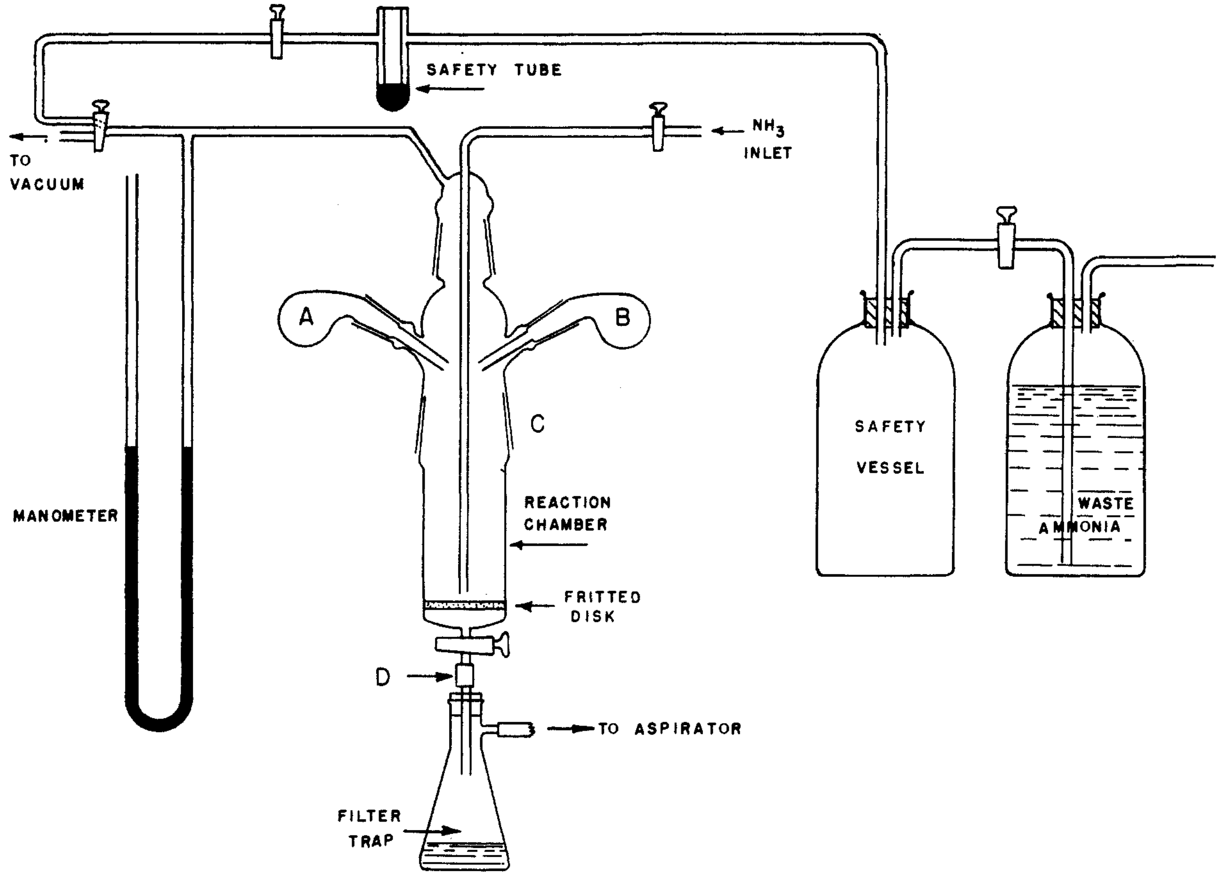

Fig. 1.—Apparatus for reactions in liquid ammonia.

sure of ammonia preventing air from entering the system during the insertion of the bulbs. The method of charging the appropriate sampling bulb with potassium was of some significance with regard to the stability of the reduction product. The most suitable method consisted of cutting the potassium under dry toluene, transferring it to a weighed bulb partially filled with toluene, and obtaining a final weighing.

After the sampling bulbs had been placed in the reaction chamber, approximately 60 ml. of ammonia was condensed by means of a Dry Ice–isopropyl alcohol bath which surrounded the chamber. By rotation of the appropriate sampling bulb, potassium, along with the toluene in which it was suspended, was introduced into the chamber. This was followed by the addition of potassium hexacyanomanganate(III). The reaction was permitted to proceed for approximately 1 hour. The liquid ammonia was then removed with an aspirator and the product washed several times with ammonia condensed by means of the Dry Ice–isopropyl alcohol bath. A thin layer of ammonia was finally condensed over the yellow product; the lower part of the reaction chamber was then removed, plugged with a one-hole rubber stopper, and transferred to a dry-box which had been flushed with ammonia gas for a period of hours. Upon evaporation of the cover of ammonia, sampling operations were performed.

The reduction product prepared with potassium which had been weighed under toluene was considerably more stable than products prepared with potassium weighed under ethyl ether. Once transferred to weighing bottles in the dry-box, the color and composition of samples of the former changed relatively slowly, so that it proved possible to weigh them fairly accurately. It is entirely likely that a protective coating was formed by the toluene on the particles of the reduction product.

Analytical Methods.—The analytical methods described below were tested on synthetic mixtures containing potassium cyanide and manganese(II) sulfate of known purity, and gave satisfactory results. Bound ammonia was determined by the Kjeldahl method.

The analysis for cyanide was carried out in one of two ways. In a modification of the method described by Bigelow,[6] the sample was distilled with dilute sulfuric acid, and a quantity of the distillate was caught in dilute sodium hydroxide solution cooled in an ice-bath. The resulting solution was acidified and titrated with standard silver nitrate solution in the presence of potassium iodide as indicator. In a second method, the sample in aqueous suspension was made ammoniacal and about 95% of the quantity of silver nitrate solution required to react with the cyanide was added. The oxide of manganese which formed was removed by filtration, and the clear filtrate containing the cyanide was titrated to an end-point with potassium iodide serving as indicator.

After removal of cyanide by sulfuric acid treatment and distillation, potassium was determined as the sulfate in the following manner. The remaining solution was made ammoniacal, buffered with an ammonium salt, and saturated with hydrogen sulfide. The mixture was permitted to stand for at least one day to permit coagulation of the manganese sulfide precipitate. The precipitate was then filtered through a fritted-glass filter of medium porosity and the filtrate treated with sulfuric acid, evaporated to dryness, and ignited at 1000°.

Manganese was determined, after removal of cyanide as hydrogen cyanide, by the bismuthate method, under the optimum conditions described by Cunningham and Coltman.[7]

Measurement of Reducing Power of Product.—The oxidation state of the manganese in the yellow complex formed by the reduction of potassium hexacyanomanganate(III) with potassium was found by measuring its reducing power toward an excess of an ammonia solution of silver nitrate. This was accomplished in the manner described below, after it had been demonstrated that the yellow reduction product

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[6] J. H. Bigelow, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 204.

[7] T. R. Cunningham and R. W. Coltman, *Ind. Eng. Chem.*, **16**, 58 (1924).

was practically insoluble in liquid ammonia. The assumption was made that the potassium hexacyanomanganate(III) was quantitatively converted to the yellow product by potassium.

The reduction product was prepared in the usual manner, care being taken, however, to keep the level of liquid ammonia below the standard taper joint C. After reaction was complete and solvent had been removed, the product was washed at least twice with liquid ammonia to remove excess potassium. Solid silver nitrate, in excess of 4.5 moles per mole of starting complex (this allowed 1.5 moles for the reduction and at least 3 moles for combination with the 6 cyanide groups), was placed in a clean dry sampling bulb. The bulb was flushed with ammonia gas, permitted to cool to room temperature, and inserted into the system. The silver nitrate was then washed into the reaction chamber by condensing ammonia in the bulb.

The silver nitrate and the reduction product were permitted to react for approximately one-half hour, stirring being effected by means of a stream of ammonia gas which was constantly bubbled through the reaction chamber. To obtain quantitative reduction of silver ion it was necessary occasionally to detach the lower part of the reaction chamber and thoroughly stir the liquid ammonia suspension with a sharp pointed glass rod, especially in the cracks around the fritted-glass disk. The solvent was removed by aspiration and the residue washed several times with liquid ammonia to remove excess silver nitrate and any silver cyanide, simple or complex, which may have been present. This was followed by at least two washings with distilled water, and then by treatment with dilute hydrochloric acid to remove manganese and free cyanide ion. The residue of finely divided silver was dissolved in hot dilute nitric acid and silver was determined in the solution by precipitation as chloride.

Magnetic Susceptibility Measurements.—The paramagnetic susceptibility of the yellow reduction product was determined by the Gouy method, correction being made for the diamagnetic contributions of ammonia, and of potassium and cyanide ions. All sampling operations were performed in a dry-box in which was maintained an ammonia atmosphere.

Results and Discussion

In a study of the ratio by weight in which potassium and potassium hexacyanomanganate(III) reacted with each other, it was found, surprisingly, that the blue color due to excess potassium persisted in the solution for more than a few minutes only when more than 2.5 atoms of potassium were added per mole of complex. This fact suggested that the stoichiometry of the reaction might be represented by the equation

$$2K_3Mn(CN)_6 + 5K = K_5Mn(CN)_6 + K_6Mn(CN)_6$$

and that the product might contain unipositive and zero manganese, atom for atom.

The yellow reduction product, which contained some ammonia which was slowly lost on standing, was subjected to complete analysis. The ratio K:Mn:CN:NH$_3$ as calculated from the analytical data (mean of several determinations of each constituent on freshly prepared samples) was 5.42:1:5.93:1.11. These results indicate a product of the empirical formula $K_{11}Mn_2(CN)_{12}\cdot 2NH_3$, as may be seen also from the analyses.

Anal. Calcd. for $K_{11}Mn_2(CN)_{12}\cdot 2NH_3$: K, 48.53; Mn, 12.40; CN, 35.23; NH$_3$, 3.84. Found[8]: K, 48.29; Mn, 12.51; CN, 35.11; NH$_3$, 4.29.

The reducing power of the product, as determined by reaction with silver nitrate, gave results in complete accord with the analytical data. Values of the reducing power (in gram-atoms of silver per gram-atom of manganese) in four experiments were 1.52, 1.50, 1.53, and 1.55. Since the manganese was oxidized by silver ion to the dipositive state (experiments showed that manganese(II) in the presence of excess cyanide ion is not oxidized by silver ion in liquid ammonia), the reducing power experiments definitely point toward an initial mean oxidation state of one-half for manganese.

As might be expected of a substance containing manganese in the zero oxidation state, the reduction product was found to be distinctly paramagnetic. When the molar weight was calculated on the basis of the formula $K_{11}Mn_2(CN)_{12}\cdot 2NH_3$, the mean of five values (1.29, 1.22, 1.20, 1.37 and 1.17) found for the effective magnetic moment was 1.25 Bohr magnetons, as compared to a calculated value for one unpaired electron of 1.73 Bohr magnetons. The discrepancy, however, is less serious than it might at first appear, since a very slight degree of oxidation of the product (which, in view of the instability of the product toward atmospheric oxidation and the difficulty of sampling, is almost unavoidable) would appreciably lower the value of the effective magnetic moment. Thus a mixture of 40 mole % of zero manganese compound and 60 mole % of the unipositive manganese compound would have a theoretical moment of the same magnitude as that found experimentally.

The substantial concordance of the four lines of evidence described above may, it appears to us, best be explained on the hypothesis that the reduction product contains manganese in both the unipositive and the zero oxidation state, in at least approximately the atomic ratio 1:1. Its composition may perhaps best be represented by the formula $K_5Mn(CN)_6\cdot K_6Mn(CN)_6\cdot 2NH_3$.

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[8] In the following summary of results of individual analyses, the first figure, in each case, is for K, the second for Mn, the third for CN, the fourth for NH$_3$. (1): 47.92, 12.33, 34.64, 3.71. (2): 48.00, 12.38, 34.86, 4.48. (3): 48.13, 12.46, 35.09, 4.69. (4): 48.33, 12.49, 35.12, ... (5): 48.64, 12.52, 35.46, ... (6): 48.71, 12.69, 35.48, ...