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# Manganese Nitrosyl Cyanide Salts

BY ARTHUR A. BLANCHARD AND FREDERICK S. MAGNUSSON

A study of the metal carbonyls and nitrosyl carbonyls has revealed that for all volatile compounds of this class the effective atomic number (E. A. N.) is the same as the atomic number of one of the inert gases.[1]

Furthermore, a study of Werner complexes particularly of the complex cyanides and the carbonyl and nitrosyl substituted complex cyanides has shown an unmistakable trend toward greater stability when the E. A. N. of the central atom is the same as the atomic number of an inert gas.[2]

Manchot and Gall[3] and Manchot and Schmid[4] have succeeded in preparing the very unusual compounds $M_5[Mn(CN)_6]$ and $M_3[MnNO(CN)_5]$ where M stands for a univalent alkali metal. The ability of such unexpected complex ions as $Mn(CN)_6^{-----}$ and $MnNO(CN)_5^{---}$ to exist at all would seem to depend on the stabilizing effect of the E. A. N. of 36 (krypton).

We have repeated the preparation of $K_3[MnNO(CN)_5]$ by the method of Manchot and Schmid and have confirmed their results; we have modified their method until we have obtained a yield of 70 instead of 15%, and we have studied some of the properties of the complex ion and its salts.

Manchot and Schmid prepared the salt by shaking a water–alcohol solution of $Mn(C_2H_3O_2)_2$ and potassium cyanide in the ratio of 1:5 in an atmosphere of nitric oxide

$$NO + Mn(C_2H_3O_2)_2 + 5KCN \longrightarrow K_3[MnNO(CN)_5] + 2KC_2H_3O_2$$

and then by careful addition of alcohol precipitating first the excess of potassium cyanide and then with more alcohol precipitating the complex salt in a reasonable state of purity.

According to our improved method potassium hydroxide is added to the mixture, which suppresses the formation of the green precipitate of $KMn(CN)_3$ and facilitates the absorption of nitric oxide. A complete separation of an insoluble salt of the complex is then accomplished by the addition of excess $Mn(C_2H_3O_2)_2$ and $HC_2H_3O_2$. The manganous salt is a bright rose granular precipitate which filters easily. Treatment of this with concentrated potassium carbonate yields insoluble manganous carbonate and a pure solution of $K_3[MnNO(CN)_5]$

$$Mn_3[MnNO(CN)_5]_2 + 3K_2CO_3 \longrightarrow 2K_3[MnNO(CN)_5] + 3MnCO_3$$

Careful addition of alcohol to the filtrate from the manganous carbonate causes the formation of deep purple crystals of the pure salt.

**Details of Preparation.**—Fill the shaking vessel with nitric oxide and introduce in order 0.02 F. W. $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ (4.9 g.) in 25 cc. of water, 0.02 F. W. KOH (1.3 g.) in 25 cc. of water, 0.10 F. W. KCN (6.5 g.) in 25 cc. of water, and shake for four and one-half hours. Nearly 500 cc. of nitric oxide, *i. e.*, about the theoretical amount, will be taken from the reservoir. The green precipitate at first formed ($KMn(CN)_3$) gradually disappears and the solution becomes a deep red-purple, resembling the color of permanganate. There is a small amount of light colored residue ($Mn(OH)_2$). Remove the nitric oxide from the shaker, then pour the solution into a beaker, add 7.0 g. of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$, stir, and add slowly with stirring 10 cc. of 6 *N* $HC_2H_3O_2$. Stir frequently for one-half hour and collect the rose precipitate on a filter and wash it with water. Digest this precipitate with 4.0 g. of potassium carbonate dissolved in 15 cc. of water, warming gently. Pour on a filter and wash the residue on the filter with a mixture of 10 cc. of water and 30 cc. of alcohol. Add acetic acid carefully to the filtrate until evolution of carbon dioxide ceases. Add 100 to 150 cc. of alcohol and let the solution stand overnight. Deep purple hydrated crystals are obtained which may be washed with alcohol; yield 5.0 g. or 70%.

**Analysis.**—The preparation was dried to constant weight over phosphorus pentoxide, whereby it fell to a light blue powder. Nitrogen and carbon were determined by Mr. J. Kovitz, professional analyst at the Massachusetts Institute of Technology, and manganese and potassium were determined by Magnusson as sulfates after separation with ammonium sulfide.

| | Calculated for $K_3MnNO(CN)_5$ | Found | |
|---|---|---|---|
| Nitrogen | 25.30 | 25.7 | 25.9 |
| Carbon | 18.06 | 17.8 | 17.5 |
| Manganese | 16.53 | 16.56 | 16.64 |
| Potassium | 35.30 | 35.55 | 35.36 |
| Oxygen by difference | 4.81 | 4.5 | |

The analyses thus give the atomic ratios as Mn, 1.000; K, 3.03; C, 4.86; N, 6.10; O, 0.93.

**Chemical Behavior.**—The dry preparation of potassium manganese nitrosyl cyanide either hydrated or anhydrous appears to be perfectly stable when in a closed container in

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(1) Blanchard, *Chem. Rev.*, **21**, 3 (1937).

(2) Blanchard, *ibid.*, **26**, 409 (1940).

(3) Manchot and Gall, *Ber.*, **61**, 1135 (1928).

(4) Manchot and Schmid, *ibid.*, **59**, 2360 (1926).

the absence of light. In water the salt produces a red permanganate-colored solution. The water solution becomes turbid after a day, and a black film collects on the walls of the glass vessel. Nitric, sulfuric and hydrochloric acids in 2 *N* concentration have no immediate effect on the water solution but after about two hours the color begins to change to a strong yellow. Saturated sulfurous acid shows no effect in two hours. The color changes slowly in the cold in ammonium and sodium hydroxide solutions; rapidly when heated. Dilute ammonium sulfide does not affect the color but a concentrated solution produces a brown-red color. Metal salt solutions produce characteristic precipitates in solution about 1 *N* in nitric, sulfuric or hydrochloric acid.

| Metal salt | Character of precipitate |
|---|---|
| Aluminum | None |
| Cadmium | Pale rose |
| Cobalt | Purple-brown |
| Copper | Brown-violet |
| Iron(ic) | Deep green solution; color visible at dilution of 1:100,000 |
| Iron(ous) | Dirty brown |
| Lead | None |
| Manganese | Rose |
| Mercury(ic) | Rose |
| Nickel | Blue-gray |
| Zinc | Brilliant rose; does not settle |

**Results of Attempts to Prepare Analogous Cobalt Salts.**—The salt under discussion is the manganese analog of the well-known nitroprusside of iron $K_2[Fe(CN)_5NO]$. In the latter, the E. A. N. of iron is 36 as it also is in the somewhat less well-known carbonyl substituted complex cyanide $K_3[Fe(CN)_5CO]$.[5] The cobalt analogs of these iron compounds would be $K[Co(CN)_5NO]$ and $K_2[Co(CN)_5CO]$. We have attempted to prepare them by starting with a black suspension of cobaltic oxide (mixture of $Co_2O_3$ and $CoO_2$) prepared by adding sodium hydroxide and sodium hypobromite to a solution of cobaltous salt and washing by decantation. Potassium hydroxide is added to distinct alkalinity, then potassium cyanide in a ratio to Co of 5:1 and the suspensions are saturated with nitric oxide and carbon monoxide, respectively. We might expect the following reactions to occur

$$CoO_2 + 5KCN + NO + 2H_2O \longrightarrow K[Co(CN)_5NO] + 4KOH$$

$$Co_2O_3 + 10KCN + 2CO + 3H_2O \longrightarrow 2K_2[Co(CN)_5CO] + 6KOH$$

Actually, nitric oxide and carbon monoxide are absorbed very rapidly in these experiments, but the hoped for compounds could not be identified among the products. However, the expectation of obtaining products in which cobalt has the E. A. N. of 36 was amply realized, for potassium cobalticyanide, $K_3[Co(CN)_6]$ and the potassium salt of cobalt carbonyl hydride, $K[Co(CO)_4]$, respectively, were found in abundance.

## Summary

The general tendency of elements to acquire the effective atomic number of the nearest inert gas apparently does not hold in the formation of simple compounds of the heavy metals. However, a study of the complex compounds of the heavy metals does reveal an obvious tendency of this kind. This is shown in the long-known sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, and in the manganese compounds, $K_3[Mn(CN)_5NO]$ and $K_5Mn(CN)_6$.

The composition of the potassium manganese nitrosyl cyanide has been confirmed, an improved method of preparation has been devised, and its reactions have been recorded.

Attempts to prepare analogous substituted complex cyanides of cobalt, $K[Co(CN)_5NO]$ and $K_2[Co(CN)_5CO]$, did not succeed in the direct objective, but they did succeed in the formation of previously known compounds, $K_3[Co(CN)_6]$ and $K[Co(CO)_4]$, respectively, in which the E. A. N. of cobalt is 36.

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(5) Manchot and Woringer, *Ber.*, **45**, 2869 (1912); **46**, 3514 (1913).