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THE PREPARATION AND PROPERTIES OF A NEW PENTACYANOMANGANESENITRIC OXIDE ANION, $[Mn(CN)_5NO]^{2-}$, AND SOME OBSERVATIONS ON OTHER PENTACYANONITROSYL COMPLEXES

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Abstract—The yellow anion $[Mn(CN)_5NO]^{2-}$ may be prepared by oxidizing the purple $[Mn(CN)_5NO]^{3-}$ with $\sim$6 N nitric acid in aqueous solution. Various salts may be isolated among which the silver, potassium and zinc salts have been prepared in pure form. The anion and its salts are only moderately stable. The silver and potassium salts are magnetically anomalous in the solid state; whereas the zinc salt in the solid state has a magnetic susceptibility corresponding to $\mu_{\text{eff}} = 1{\cdot}86$ BM. A magnetic susceptibility corresponding to $\mu_{\text{eff}} = 1{\cdot}76$ BM. was also obtained for the potassium salt in acetone solution. Infra-red and ultra-violet spectra of the ions $[Mn(CN)_5NO]^{2-}$, $[Mn(CN)_5NO]^{3-}$ and several cyano anions isoelectronic with the latter are reported and discussed.

Nitric oxide co-ordinates readily with metals forming a bewildering variety of compounds(1) which are for the most part of uncertain structure, especially in regard to the manner in which the NO group is bound. To date, however, only three pentacyanonitrosyl complex anions of metals of the first transition series have been reported, viz. salts of $[Mn(CN)_5NO]^{3-}$, $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_5NO]^{3-}$. The nature of the last-mentioned is very uncertain(2) and it will not be further discussed here. The first two are isoelectronic and diamagnetic, and it has been proposed that they may be regarded as consisting of Mn^+, $5CN^-$, NO^+ and Fe^{2+}, $5CN^-$, NO^+ respectively.(3) The metal-NO bond is thus represented as a resonance hybrid of $M^- \leftarrow NO^+$ and $M \rightleftarrows N{=}O$.

In this paper we report the existence of a new, moderately stable complex ion, $[Mn(CN)_5NO]^{2-}$. The chemical, magnetic and spectral properties of this ion as well as of $[Mn(CN)_5NO]^{3-}$ and $[Fe(CN)_5NO]^{2-}$ have been studied in some detail. The new ion is the first pentacyanonitrosyl anion with an odd number of electrons to be fully characterized.

EXPERIMENTAL

Preparation of $K_3[Mn(CN)_6]$. Two principal methods have been described for the preparation of this compound. One is a two-step synthesis involving first the preparation of $MnPO_4{\cdot}H_2O$ in relatively low yield (50–80 per cent) and then the conversion of this to the desired compound in good yield (90–95 per cent).(4) Meyer has also reported that it may be prepared directly by *in situ* oxidation of $K_4Mn(CN)_6$ with a current of air.(5) He reported yields of $\sim$90 per cent. We have reinvestigated the Meyer procedure and find that with certain slight modifications yields of $\sim$95 per cent can be

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(1) For a partial listing see J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. Nucl. Chem.* **7**, 32 (1958).

(2) N. V. Sidgwick, *The Chemical Elements and Their Compounds.* Vol. 2. p. 1343 Oxford University Press (1950).

(3) D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N.S.W.* **78**, 25 (1944).

(4) J. A. Lower and W. C. Fernelius, *Inorganic Syntheses* Vol. 2, p. 213. McGraw-Hill, New York (1946).

(5) J. Meyer, *Z. anorg. Chem.* **81**, 390 (1913).

consistently obtained. Thus it appears more satisfactory than the two-step procedure. Good yields require attention to the following points:

(1) The $MnCO_3$ must be added to the KCN solution in small portions over at least 30 min. It should be finely powdered and any lumps which form in the reaction mixture should be crushed. This is necessary to provide maximum contact of the air stream with the $K_4Mn(CN)_6$ initially formed.

(2) A vessel about twice the size suggested by MEYER and the use of ~25 per cent more water facilitates the oxidation step. An oxidation period of ~24 hr was found adequate if the above suggestions are followed.

(3) Neither the reaction mixture nor solutions used in recrystallization should be heated above 80° because this causes decomposition to Mn(III) hydroxide. Rapid cooling during recrystallization tends to give a blue slimy deposit, difficult to filter. The product is actually pure enough for further synthetic use without recrystallization and was used directly for the preparation of $K_3[Mn(CN)_5NO]$.

The only aspect of the above procedure which might, in some circumstances, be undesirable is the 24 hr waiting period for air oxidation to occur. With a sacrifice in yield this may be avoided by oxidizing the $K_4Mn(CN)_6$ with $KMnO_4$, according to the reaction

$$MnO_4^- + 3Mn(CN)_6^{4-} + 2H_2O \rightarrow 3Mn(CN)_6^{3-} + 4OH^- + MnO_2.$$

An excess of an ice cold solution (2·5 g/100 ml) of $KMnO_4$ was added slowly, with vigorous stirring to the slurry of $K_4Mn(CN)_6$ also containing excess KCN cooled to 0°. After warming to room temperature the mixture was stirred for a further 15 min and filtered. The filter cake consisted chiefly of $K_3Mn(CN)_6$ but contained some MnO_2. The product was purified by recrystallization from 10 % KCN solution as in the MEYER method. The yield was ~75 per cent based on $MnCO_3$ used.

Preparation of $K_3[Mn(CN)_5NO]$. The literature contains three reports of preparations of this compound. It was first prepared in 1926 by MANCHOT and SCHMID(6) in very poor yield by passing nitric oxide into a solution containing manganous ion and potassium cyanide. BLANCHARD and MAGNUSSON(7) in 1941 reported a greatly improved yield when KOH was added to the reaction mixture. In 1948, HIEBER *et al.*(8) reported preparing the compound by treating $K_3Mn(CN)_6$ with a basic solution of hydroxylamine. Although the principles of this method are sound the directions given were vague and yields of no more than 70 per cent of somewhat impure material were at first obtained by us. The following procedure gives about an 85 per cent yield of very pure material.

Twenty grams of $K_3[Mn(CN)_6]$ are finely powdered and slowly stirred into 66 ml of a 10 per cent potassium cyanide solution so that the particles remain agitated and do not form a cake at the bottom. 87 g of a 10 per cent solution of hydroxylamine (made basic with KOH) is then added to the slurry and the mixture maintained at 75° for 15 min. The mixture is then filtered to remove $Mn(OH)_3$ and other solids. Glacial acetic acid is added to the filtrate until it is acid after which 830 ml of filtered, saturated solution of manganous acetate is added to precipitate $Mn_3[Mn(CN)_5NO]_2$. The manganous acetate should be added slowly with constant stirring in order to obtain an easily filterable precipitate which is filtered off after 30 min. The final yield may be increased from ~75 per cent to ~85 per cent if the filtrate from precipitation of $Mn_3(MnCN)_5NO]_2$ is slowly treated with one quarter of its volume of methanol, filtered after 10 min and the additional precipitate added to the first crop. The entire precipitate is washed with 100 ml of 50 per cent ethanol followed by 25 ml of 95 per cent ethanol and then ether and air dried.

The manganous salt, $Mn_3[Mn(CN)_5NO]_2$, is weighed and then mixed with sufficient 40% K_2CO_3 solution to give a 10 per cent excess of K_2CO_3 according to the equation

$$Mn_3[Mn(CN)_5NO]_2 + 3K_2CO_3 = 3MnCO_3 + 2K_3[Mn(CN)_5NO].$$

This paste is digested for 45 min with constant mixing and filtered with suction. The cake of $MnCO_3$ is washed with a volume of 50 per cent ethanol equal to one half the volume of the filtrate. The combined filtrate and washings are acidified with glacial acetic acid added slowly with stirring. The product is precipitated by adding 95 per cent ethanol, in about ten times the volume of the acidified filtrate, slowly over about 15 min. The precipitate and liquors are left to stand for 10–12 hr (on longer standing decomposition takes place), filtered and the precipitate washed with 95 per cent ethanol. The product is recrystallized by dissolving it in three tımes its weight of water; the solution is filtered

(6) W. MANCHOT and H. SCHMID, *Ber. Dtsch. Chem. Ges.* **59** *B*, 2360 (1926).

(7) A. A. BLANCHARD and F. S. MAGNUSSON, *J. Amer. Chem. Soc.* **63**, 2236 (1941).

(8) W. HIEBER, R. NAST, E. PROESCHEL and R. SCHUK, *Z. anorg. Chem.* **256**, 159 (1948).

and five times the volume of 95 per cent ethanol slowly added. This produces a crystalline precipitate which may be filtered after standing 2 hr and is then washed with 95 per cent ethanol and ether and air dried. This recrystallized product is markedly purer than that produced by the original HIEBER method in our hands. Yields were 80–90 per cent.

The dihydrate may be dehydrated by drying overnight in a vacuum with P_2O_5. For the hydrate, a weight loss on drying over P_2O_5 corresponding to 9·93% H_2O was found which is in agreement with the dihydrate formula reported by HIEBER (theory, 9·78 per cent). The anhydrous material gave the following analysis. (Found: K, 35·16, 35·20; Mn, 16·59, 16·65; C, 18·45, 16·80; N, 25·47, 24·97; CN, 39·00, 39·06. Calc.: K, 35·30; Mn, 16·53; C, 18·07; N, 25·31; CN, 39·14%). The direct carbon analysis is unreliable due to poor combustion of the compound even in the presence of $K_2Cr_2O_7$.

Reactions of $[Mn(CN)_5NO]^{3-}$. The hydrated and unhydrated solids are stable for at least three months in darkness or diffuse light, but after one week in air and strong sunlight there is considerable surface decomposition.

Solutions of the potassium salt, in the presence of air are attacked after a few minutes by ammonia and caustic alkalis. A precipitate of MnO_2 appears and increases steadily but even after two months the reaction is not complete at room temperature. At 100° reaction is complete within a few minutes. In the absence of air 6 N alkali hydroxides are virtually without effect at 80° for three days. Concentrated KCN solution is without effect. Stannous chloride and stannites have no effect. The precipitation reactions with heavy metals are essentially as reported by BLANCHARD.(7)

Silver ions give an initially pink precipitate which quickly turns white. An infra-red spectrum of the precipitate showed two peaks at ~2175 and ~2060 cm^{-1} due to CN stretches but no absorption at all between 1500 and 2000 cm^{-1}. Probably the silver ions destroy the anion, precipitating mainly AgCN. Ferric ions give a green-black precipitate which has strong absorptions at ~2110 and 1800 cm^{-1} suggesting (see discussion of spectra of other salts of the anion) perhaps that $Fe[Mn(CN)_5NO]$ is precipitated.

The action of acids is complex. Previous statements(8) failing to distinguish between the action of different acids are misleading. The acids studied here were hydrochloric, sulphuric, phosphoric, perchloric, acetic and nitric. At room temperature all these acids, except nitric, at concentrations up to 6 N, produce a red solution in 5 min or less and in the case of perchloric, a precipitate of $KClO_4$. The addition of alkali instantly reverses this colour change. These red solutions give precipitates with many heavy metal ions which appear to be identical with the corresponding precipitates of the $[Mn(CN)_5NO]^{3-}$ ion. It is therefore, probable that the red colour is due to a protonated form of that ion. The red ion cannot be extracted into ether. After about ½ hr at 80° or 24 hr at room temperature the red colour lightens through various shades of orange becoming finally bright yellow. Addition of alkali to this solution causes complete decomposition to hydroxides of manganese. During a few more hours at 80° or another day at room temperature the yellow colour fades slowly, finally leaving a colourless solution of the manganous ion. The yellow species could not be isolated by precipitation with heavy metal ions because the continuously changing nature of the solution made it uncertain when the precipitates were no longer due to the $[Mn(CN)_5NO]^{3-}$ ion or the red ion. Also it was not extracted by ether. HCN is continuously evolved during these changes.

The action of nitric acid is unique. If 6 N nitric acid is boiled and cooled it produces the same reddening effect at room temperature, but the solution suddenly turns an intense yellow after a few minutes at room temperature or immediately on warming. If the concentration is 8 N, the yellow colour is produced at room temperature without the induction period. Also concentrated nitric acid which is quite yellow (i.e. containing nitrogen oxides) when diluted even to 4 N produces the yellow colour instantly at room temperature. As shown below, this yellow colour is due to the ion $[Mn(CN)_5NO]^{2-}$. The dependence of the ease of oxidation on the presence of lower-valent nitrogen compounds suggest that they act as intermediates in the oxidation.

Acids more concentrated than 6 N break down the complex producing cloudy solutions and precipitates and ultimately the manganous ion. Sulphuric acid is especially efficient and quite useful for decomposition prior to analysis.

Solutions of $[Mn(CN)_5NO]^{3-}$ are decolorized by neutral hydrogen peroxide, turned red by basic peroxide and oxidized to $[Mn(CN)_5NO]^{2-}$ by acidic peroxide. All of these changes are reversed on addition of stannous or stannite ion or formic acid.

Preparation of $Ag_2[Mn(CN)_5NO]$. This compound was prepared by oxidation of $[Mn(CN)_5NO]^{3-}$

with nitric acid and precipitation of the salt by addition of Ag^+. Five grams of anhydrous $K_3[Mn(CN)_5NO]$ were dissolved in 15 ml of water at 0° and the solution filtered through a fine sintered glass disk. Twenty-five millilitres of yellow nitric acid (15·6 N) were diluted to 50 ml, cooled to 0° and added to the solution causing it to turn dark red. When allowed to warm to room temperature with stirring the solution turned yellow and oxides of nitrogen were evolved. The solution was then diluted to 120 ml, filtered if not clear, and 330 ml of 0·1 N $AgNO_3$ solution (10 per cent excess) added over a period of ~5 min with stirring. The precipitate was light brown to flesh-coloured and was allowed to stand with the supernatant liquid for 15 min. The supernatant liquid was then removed by suction filtration using a hardened filter paper. It was then washed successively with 10 ml each of water, ethanol and ether, all at 0°, and dried 2 hr with P_2O_5 in vacuum. It was ground in an agate mortar and redried in the same way for an additional 2 hr. Further drying causes no further weight loss. (Found: Ag, 49·72, 50·08; Mn, 12·76, 12·60; C, 14·54; N, 19·29; CN, 30·05, 30·15. Calc. for $Ag_2[Mn(CN)_5NO]$: Ag, 50·08; Mn, 12·75; C, 13·94; N, 19·51; CN, 30·19%).

Preparation of $Zn[Mn(CN)_5NO]\cdot XH_2O$. This salt was prepared in the same way as the silver salt up to the point at which the yellow solution containing nitric acid came to room temperature. The solution was then filtered if not clear but was *not* diluted since the zinc salt is moderately soluble. One and a half grams of $Zn(NO_3)_2$, as a saturated solution in water (5 per cent excess), were added producing a bright yellow precipitate which was then washed and dried as was the silver salt. The zinc salt was not anhydrous even when kept in vacuum for extended periods over P_2O_5. The water content varied somewhat. A typical preparation gave the following analysis. (Found: Zn, 20·36, 19·94; Mn, 16·33, 16·29; C, 17·78; N, 24·21; H, 1·96. Calc. for $Zn[Mn(CN)_5NO]\cdot 3{\cdot}3\,H_2O$: Zn, 19·24; Mn, 16·16; C, 17·67; N, 24·73; H, 1·96%).

Preparation of $K_2[Mn(CN)_5NO]$. Five grammes of $K_3[Mn(CN)_5NO]$ were dissolved in 15 ml of water and the solution filtered through a fine sintered glass disk. Yellow conc. nitric acid (15·6 N) was added dropwise (or, alternatively, 1·2 g bromine in 50 ml of ether was added slowly with agitation) to accomplish oxidation. The solution was swirled gently for 5 min as it became bright yellow and N_2O_4 was evolved. The solution was then evaporated to dryness by pumping while heating it to ~70° in a water bath. After about 4 hr of pumping the residue appeared quite dry and was yellow brown in colour. It was then scraped from the flask, ground in an agate mortar and stored in vacuum over P_2O_5 for 24 hr.

Five hundred millilitres of analytical reagent grade acetone, dried with magnesium sulphate then potassium carbonate, were siphoned into a thoroughly dry distillation apparatus. The first 100 ml of distillate were rejected and the next 200 ml were distilled directly into a dry 300 ml flask containing the crude, dry product and fitted with a drying tube to exclude water vapour. The mixture of acetone and powder was then shaken for 1 hr, the supernatant liquid siphoned off through a glass wool plug into a 500 ml suction flask and reduced to ~60 ml by vacuum evaporation. The solution at this point was usually clear yellow but when cloudy was filtered by suction as rapidly as possible through a hard paper. One hundred millilitres of sodium-dried ether were then added slowly to the acetone solution through a siphon. A brilliant canary-yellow, flocculent precipitate then formed and after 5 min it was filtered off by suction through a hardened paper as rapidly as possible, immediately washed on the paper with a mixture of 15 ml of dry acetone and 25 ml of dry ether and quickly placed in a vacuum desiccator with P_2O_5. This final filtration and washing must be done rapidly because atmospheric water vapour turns the edges of the filter cake brown within about 5 min. It was found that a small additional quantity of product could be isolated from the final yellow filtrates by evaporating to ~10 ml and adding ether, but the amount so obtained was hardly worth the effort. Yields averaged 40 per cent using either nitric acid or bromine as oxidant. (Found: K, 26·58, 26·55; Mn, 18·78, 18·85; C, 19·92; N, 29·84; CN, 44·50, 44·55. Calc. for $K_2[Mn(CN)_5NO]$: K, 26·67; Mn, 18·74; C, 20·48; N, 28·67; CN, 44·36%).

Chemical Properties of $[Mn(CN)_5NO]^{2-}$ *and its salts.* The ion in aqueous solution gives precipitates with the following other cations: mercurous (flesh coloured), cupric (light green), ferrous (dark green), nickelous (light yellow), cobaltous (red). The constitution of these precipitates has not been investigated.

The potassium salt is very soluble in water and quite soluble in ethanol. These solutions become cloudy within a few minutes. It is sparingly soluble in anhydrous acetone and the solutions are stable for periods from 0·5 to 2 hr. Solutions in dilute nitric acid remain clear for hours but this may only be due to solubility of the decomposition products.

The silver salt seems to decompose spontaneously though slowly at room temperature evolving nitric oxide. It is slightly soluble in water but quickly decomposes to silver cyanide, manganous ions and other doubtful products.

The $[Mn(CN)_5NO]^{2-}$ ion can be reduced to $[Mn(CN)_5NO]^{3-}$ by stannous ions, stannites, formic acid, etc. Addition of alkali to the acidic solution causes it to turn red and this may be reversed by reacidification. The red alkaline solution is reduced with loss of colour by alkaline reducing agents and again turns red on addition of alkaline oxidizing agents. Evaporation of the red solution gave a complex mixture of solids apparently containing MnO_2 and $K_3[Mn(CN)_5NO]$.

Preparation of $K_3[Fe(CN)_5CO]\cdot 0{\cdot}6\ H_2O$. Two methods for the preparation of this compound are given in the literature.(9,10) The method of Hieber *et al.*, calls for conversion of the nitroprusside ion to the pentacyano-aquo ion followed by treatment of an aqueous solution of this with carbon monoxide. We were unable to isolate any of the desired product by this method. The second method involves the reaction of a ferrocyanide solution with carbon monoxide under pressure and high temperature according to the equation:

$$K_4Fe(CN)_6 + 2H_2O + CO \rightarrow K_3[Fe(CN)_5CO] + HCOOK + NH_3$$

The published description of this method is rather vague; some of the details of our procedure are therefore given here.

Twenty-five millilitres of a saturated aqueous solution of $K_4Fe(CN)_6\cdot 3H_2O$ contained in a glass tube were placed in a steel pressure bomb. The bomb was charged with CO to 1000 lbs/in^2 and then heated to 300°C for 24 hr. After opening the bomb the solution was filtered and crude product precipitated by addition of ethanol. Purification was accomplished by recrystallizations which were carried out quickly in semi-darkness to minimize photochemical decomposition. The crude product was dissolved in ~10 ml of water, the solution made slightly acid with acetic acid and ethanol added to reprecipitate the product. This effectively frees it of potassium formate. It was then redissolved in water and dilute NaOH added to precipitate traces of iron as $Fe(OH)_3$. After filtration, the $K_3[Fe(CN)_5CO]$ was again precipitated by addition of ethanol, washed with ether and dried overnight in vacuum with P_2O_5. Analysis showed that under such mild drying conditions 0·61 mole of water of crystallization remained. (Found: Fe, 15·7; N, 20·78; H, 0·36. Calc. for $K_3[Fe(CN)_5CO]\cdot 0{\cdot}61H_2O$: Fe, 16·32; N, 20·46; H 0·36%). (Carbon analyses by combustion were ~4 per cent low, but this is a common occurrence with materials of this nature.) The yield was ~50 per cent and could probably be improved with care in the recrystallizations.

Magnetic susceptibilities. All measurements were made with a Gouy balance using split tubes which were calibrated with either water or Mohr's salt. Low temperatures were maintained using a glass Dewar vessel with liquid nitrogen and "Dry Ice"-acetone slush as coolants. Sample temperatures were measured by means of four copper-constantan thermocouples placed on the inner wall of the jacket along the length of the sample column (~6 in).

It was found that for $K_3[Mn(CN)_5NO]$ a sample which was analytically pure was not necessarily magnetically pure. The apparent susceptibility seems to vary with the length of time between the dissolution and final drying in the recrystallization process. For a typical sample the following apparent susceptibilities of the $[Mn(CN)_5NO]^{3-}$ ion were obtained where the length of time taken for recrystallization prior to measurement is increasing in the orper given: -61×10^{-6}, -49×10^{-8}, -36×10^{-6}. The value of -65×10^{-6} given in Table 1 was reproduced several times on samples recrystallized as quickly as possible.

As the compounds $Ag_2[Mn(CN)_5NO]$ and $K_2[Mn(CN)_5NO]$ are only moderately stable they were given special handling. The $Ag_2[Mn(CN)_5NO]$ was prepared and the susceptibility determined the same day. The $K_2[Mn(CN)_5NO]$ sample was recrystallized five times from acetone just prior to the susceptibility measurements and placed in a vacuum desiccator over P_2O_5. In order to pack the tube the desiccator, weighed Gouy tube, and other sundry apparatus were placed in a polyethylene bag suitably provided with rubber gloves, gas inlet and outlet and a Plexiglass window. The open end of the bag was folded over and clamped shut using wood strips and then thoroughly flushed with pre-purified nitrogen. To insure dryness a large glass tray containing P_2O_5 was also placed in the bag. The Gouy tube was then packed in the bag and closed with a ground joint. The tube was

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(9) W. Hieber, R. Nast and C. Bartenstein, *Z. anorg. Chem.* **272**, 32 (1953).

(10) *Gmelins, Handbuch der Anorganischen Chemie*, Vol. 8, XIX, Part B, p. 740. Verlag Chemie, Berlin (1932).

weighed immediately on removal from the bag and then the joint was wax coated, after which the measurements were made.

A similar procedure was used in measuring $K_2[Mn(CN)_5NO]$ in acetone solution, the solution being prepared and the tube loaded and stoppered entirely in the dry nitrogen atmosphere. The measurements were made as quickly as possible and were completed before any detectable clouding of the solution. The entire time from initial addition of acetone to the solid to completion of the measurements averaged 15 min.

The zinc salt was packed quickly in air since it is relatively stable.

TABLE 1.—MAGNETIC SUSCEPTIBILITIES MEASURED IN THIS WORK

Compound	Temp. (°K)	Physical state	$\chi^g \times 10^6$	$\chi^{Mol.} \times 10^6$	$\chi^{Mol.} \times 10^6$ of anion[a]	$\chi^{Mol.} \times 10^6$ of metal ion[b]	μ(BM)
$K_4[Fe(CN)_6]\cdot 3H_2O$	301	Solid	−0·408	−172	−81	—	—
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	302	Solid	−0·377	−112	−76	—	—
$K_3[Fe(CN)_5CO]\cdot 0{\cdot}6H_2O$	298	Solid	−0·331	−113	−66	—	—
$K_3[Mn(CN)_5NO]$	301	Solid	−0·316	−104	−65	—	—
$Zn[Mn(CN)_5NO]\cdot 3{\cdot}3H_2O$	300	Solid	3·78	128_6	—	141_5	1·86[c]
	194	Solid	6·00	204_0	—	216_9	
	74	Solid	15·30	520_0	—	532_9	
$K_2[Mn(CN)_5NO]$	300	Acetone Sol'n	4·05	118_7	—	128_9	1·76[d]
$K_2[Mn(CN)_5NO]$	300	Solid	0·0109	3·20	—	105	0·50[e]
	196	Solid	0·0165	4·83	—	107	0·41[e]
	75	Solid	0·0421	$12{\cdot}3_4$	—	114	0·26[e]
$Ag_2[Mn(CN)_5NO]$	297	Solid	$0{\cdot}0065_7$	$2{\cdot}8_3$	—	127	0·55[e]
	193	Solid	0·0114	4·89	—	129	0·45[e]
	73	Solid	0·0279	$12{\cdot}0_4$	—	136	0·28[e]

[a] Obtained by correcting $\chi^{Mol.}$ for diamagnetism of alkali ions and water of hydration, using $\chi_{K^+}^{Mol.} = -13 \times 10^{-6}$, $\chi_{Na^+}^{Mol.} = -5 \times 10^{-6}$, $\chi_{H_2O}^{Mol.} = -13 \times 10^{-6}$.

[b] Obtained by correcting $\chi^{Mol.}$ for all diamagnetic contributions including that from Mn, using, in addition to the above, $\chi_{Zn^+}^{Mol.} = -10 \times 10^{-6}$, $\chi_{Ag^+}^{Mol.} = -24 \times 10^{-6}$, and $\chi^{Mol.}$ of an $[M(CN)_5NO]$ anion -76×10^{-6} as suggested by the diamagnetic salts listed in the table.

[c] Moment obtained from a Curie–Weiss law ($\mu = 2{\cdot}83\sqrt{[\chi_{Cor}^{Mol.}(T + \theta)]}$.) $\theta = -6{\cdot}3$°K.

[d] Calculated assuming Weiss constant, θ, equals zero.

[e] Each moment calculated as $\mu = 2{\cdot}83\sqrt{(\chi_{Cor}^{Mol.} \cdot T)}$.

Infra-red spectra. All spectra were recorded using a Perkin-Elmer Model 21 double beam spectrometer. Since the compounds studied were all insoluble in suitable organic solvents, all spectra were taken on Nujol mulls or pressed KBr disks. The great air-sensitivity of $K_2[Mn(CN)_5NO]$ necessitated special precautions in order to obtain an authentic spectrum. The Nujol mull was prepared in the nitrogen-flushed polyethylene bag (*vide supra*) and was placed in a desiccator before removal from the bag. It was then removed from the desiccator at the spectrometer and run immediately.

It was found that $Zn[Mn(CN)_5NO]\cdot XH_2O$ and, $Ag_2[Mn(CN)_5NO]$ gave very anomalous spectra when pressed in KBr disks. The spectrum of the silver salt was strongly affected even when just ground with KBr and the spectrum of the mixture run in Nujol. Similar but not quite so extreme results were obtained when the zinc salt was ground and pressed with KBr. The main effects are the appearance of a broad band at ~1800 cm^{-1}, a sharp band at ~1390 cm^{-1} and irregular changes in the CN stretching region. Grinding the silver salt with NaCl produces similar effects but not nearly so extensively. Nujol spectra of the zinc salt also consistently showed a band at ~1800 cm^{-1}. This band was always far weaker than the band at 1900 cm^{-1} (which we consider to be the authentic NO stretch) and its intensity relative to the 1900 cm^{-1} band varied noticeably. We believe that some reaction occurs between the zinc salt and the NaCl plates of the mull cell.

The reactions of these salts with alkali halides seem certainly to involve reactions of the $[Mn(CN)_5NO]^{2-}$ anion itself. Similar reactions have been observed previously with other complexes.(11,12)

Ultra-violet and visible absorption spectra. These were measured on aqueous solutions of alkali salts of the various anions using a Cary Model 17 recording spectrophotometer. Extinction coefficients were calculated from the relation $\varepsilon = D/lc$, where ε is the molar extinction coefficient, l is the cell length, c is the molar concentration of the solution and D is the optical density, viz. $\log_{10} (I_o/I)$.

DISCUSSION

General

The general physical and chemical stability of salts of the new anion $[Mn(CN)_5NO]^{2-}$ are just about sufficient to make accurate physical studies of the usual kinds feasible. The isoelectronic iron complex $[Fe(CN)_5NO]^-$ is apparently very much less stable and its isolation has not yet been reported. It seemed reasonable to consider by extrapolation that perhaps the isoelectronic chromium anion, $[Cr(CN)_5NO]^{3-}$, might be quite stable. Before attempting to prepare it however, we learned that several of its salts have recently been isolated by WILKINSON and GRIFFITH(13) and they are considerably more stable than salts of $[Mn(CN)_5NO]^{2-}$.

In the isoelectronic sequence $[Fe(CN)_5NO]^{2-}$, $[Mn(CN)_5NO]^{3-}$, $[Cr(CN)_5NO]^{4-}$, the first is extremely stable, the second moderately stable (much more so than $[Mn(CN)_5NO]^{2-}$ but the last has not yet been reported. Work directed toward its preparation has been undertaken.

Magnetic properties

Salts of $[Mn(CN)_5NO]^{-2}$. There are various *a priori* possibilities for the magnetic moment of the ion $[Mn(CN)_5NO]^{2-}$. It would certainly be reasonable to expect maximum spin-pairing, however, with ligands such as CN and NO. Thus if NO is considered to be co-ordinated as NO^+ the electronic configuration of the manganese ion would be T_{2g}^5, there would be one unpaired electron and the formal oxidation state of the manganese would be $+2$. If the NO were co-ordinated as the neutral molecule it would be possible to have only one unpaired electron in the complex (namely the one on the NO) only if the deviation from true octahedral symmetry were so great as to keep two of the three T_{2g} levels well below the remaining one. In this way the four electrons would be forced to pair up in these lower two orbitals Otherwise there would be altogether three unpaired electrons in the anion. Actually, it is found to have one unpaired electron. We think the formalism of NO^+ co-ordination is the better explanation since

(a) a large deviation from effectively octahedral symmetry does not seem likely, and,

(b) if we are to invoke the second argument in the case of $[Fe(CN)_5NO]^{-2}$ we would be led to expect two unpaired electrons, one on Fe and one on NO, whereas this ion is diamagnetic.

The statement that the ion $[Mn(CN)_5NO]^{-2}$ has one unpaired electron is based upon the magnetic moment of 1·76 BM measured on acetone solutions of the potassium salt and the moment of 1·86 BM measured on the zinc salt for which the Curie–Weiss law is followed with a very small Weiss Constant of −6·3°K. We have no

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(11) L. H. JONES and M. M. CHAMBERLAIN, *J. Chem. Phys.* **25,** 365 (1956).

(12) V. W. MELOCHE and G. E. KALBUS, *J. Inorg. Nucl. Chem.* **6,** 104 (1958).

(13) G. WILKINSON. Private Communication. To be published shortly.

definite explanation to offer for the anomalous behaviour of the solid potassium and silver salts of this anion. It does not seem possible that there would be any antiferromagnetic interaction between ions of such large size and only one unpaired electron. In order for partial pairing of spins of electrons on different anions to occur by direct interaction it must be assumed that the electron is not localized on the metal atom. Of course the idea of NO^+ co-ordination is only a formalism and it may be that the electron does have appreciable density on the NO group so that in an appropriate lattice such electrons on neighbouring anions are partially paired.

The directions for preparation of $K_3[Mn(CN)_5NO]$, especially the long period of crystallization, are intended to produce a maximum yield of product. However, the material so obtained, while analytically pure contains traces of paramagnetic impurities (unidentified). It was found that when the recrystallization was carried out as rapidly as possible the most negative susceptibility values were obtained. In order to ascertain whether the best measurements give the true susceptibility of the $[Mn(CN)_5NO]^{3-}$ ion, salts of several closely related anions were carefully measured, viz. $K_4[Fe(CN)_6]\cdot 3H_2O$, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ and $K_3[Fe(CN)_5CO]\cdot 0{\cdot}6H_2O$ which are all isoelectronic with $[Mn(CN)_5NO]^{3-}$. All of these compounds had been previously measured but it was difficult to know with what accuracy. (See footnotes to Table 1). While the value of -65×10^{-6} cgs units for $[Mn(CN)_5NO]^{3-}$ is still the lowest of the four, the variations ($-65, -66, -76, -81 \times 10^{-6}$ cgs units) are scarcely outside experimental error and moreover, while all the anions are isoelectronic small variations due to slightly differing mean radii of orbitals may well be expected. We therefore conclude that with care $K_3[Mn(CN)_5NO]$ can be obtained in a magnetically pure state and that it does not appear to be in any way magnetically anomalous.

Infra-red spectra

Recently, LEWIS *et al.*(1) have published an extensive compilation of N—O stretching frequencies for a wide variety of complexes containing NO. They have concluded that in complexes where the NO group may be regarded, *formally*, as a co-ordinated NO^+ ion, the frequency falls in the general range 1650–2000 cm^{-1} as opposed to NO groups *formally* regarded as coordinated NO^- ions, which absorb much lower, in the range 1000–1200 cm^{-1}. These generalizations will be relevant in the following discussion.

$Na_2[Fe(CN)_5NO]\cdot 2H_2O$. The spectrum of this compound has been reported before with respect to the N—O stretching frequency, LEWIS *et al.* cite 1925 cm^{-1} in KCl and 1938 cm^{-1} in KBr. We have examined the entire spectrum in the rock salt region rather carefully, including a partially deuterated specimen, since there are some uncommonly interesting features. The spectra in KBr disks and in Nujol were identical and the results are given in Table 2. The appearance of three CN stretching frequencies is exactly what would be expected for the ion $[Fe(CN)_5NO]^{2-}$ with C_{4v} symmetry. They are easily resolved. The position of the very strong NO stretching frequency at 1944 cm^{-1} is in satisfactory accord with previous observations but we believe our frequency value to be more accurate. The small splitting (see footnote (*b*) Table 2) may be due to the existence of environmentally distinguishable ions in the crystal; $\sim$12 cm^{-1} is a reasonable magnitude for such an effect.

The bands due to water of crystallization were studied in some detail because they were unusually sharp. Bands due to lattice water or co-ordinated water molecules are more commonly very broad with little or no resolution of the symmetric and asymmetric stretches. In this compound the bands are extremely sharp (the 1615 cm^{-1} is 15–20 cm^{-1} wide at half height) and strong. Comparison of the spectrum of the partially deuterated compound with the spectra of H_2O, HDO and D_2O completely confirms the assignments indicated in Table 2. It will be noted that for the water of crystallization the stretching modes all occur ~100 cm^{-1} lower than for the gaseous molecules whereas the deformation frequencies are ~20 cm^{-1} higher. These shifts are in the same directions as, but very much smaller than, those observed in crystals where the water molecules are strongly hydrogen bonded. This evidence together with the sharpness of the bands suggests strongly that the water molecules in this substance form no strong hydrogen bonds. They may well be simply trapped in interstices in the lattice so that the main effect is to restrict their rotation and thus tend actually to sharpen the bands.

TABLE 2.—THE INFRA-RED SPECTRA OF $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ AND PARTLY DEUTERATED ANALOGS

Compound	Absorption frequencies (cm^{-1})(a)				
	OH and OD str.		CN str.	NO str.	H_2O, D_2O HDO def.
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	3642	3563	2182, 2155, 2169	1944(b)	1615
$Na_2[Fe(CN)_5NO]\cdot 2(H,D)_2O$	3640	3562			1615
	2693	2630	2182, 2155, 2169	1944(b)	1182
	~3640	2654			1423
H_2O vapour(14)	3756	3652	—	—	1595
D_2O vapour(14)	2789	2666	—	—	1179
HDO vapour(14)	~3756	2719			1402

(a) Frequencies above 3000 cm^{-1} good to ±10 cm^{-1}; those below 3000 cm^{-1} good to ±3 cm^{-1}.

(b) This band may actually be double consisting of a very strong band at 1943 cm^{-1} and a strong shoulder at ~1955 cm^{-1}. Due to the breadth of the bands, this splitting is barely resolvable and cannot be said to be absolutely certain.

$K_3[Fe(CN)_5CO]\cdot 0\cdot 6H_2O$. The infra-red spectrum of this compound, which was made primarily for use in the magnetic studies, has not previously been reported. The only absorption bands in the rock salt region (other than very weak and broad humps at 3300–3700 and 1570–1630 cm^{-1} due to water) are between 1900 and 2150 cm^{-1}. The CO stretching frequency is apparently stronger and broader than the CN stretching frequencies and the absorption in this region is not well resolved. It can be described as follows: 1990 (shoulder, medium), 2035 (shoulder, strong), 2052 (broad, strong), 2082 (strong), 2102 (sharp, strong).

$K_3[Mn(CN)_5NO]\cdot 2H_2O$. The NO stretching frequency is broad with a rather irregular shape suggestive of several shoulders separated by somewhat less than the least resolvable separation. The band has a rather sharp peak at 1725 ± 5 cm^{-1}, LEWIS *et al.* report 1730 cm.* Absorption in the CN stretching region consists of a

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* For what they listed as the anhydrous compound but which we assume to have been the hydrate (see next section).

(14) See G. HERZBERG, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules* pp. 280–282. Van Nostrand, New York (1945).

strong sharp peak at 2100 ± 10 cm with shoulders at ~2060 and 2138 ± 10 cm^{-1} The water of crystallization gives relatively broad peaks at 3240, 3370, a fairly sharp peak at 3580 with indications of other unresolved peaks in this region and a rather broad and bumpy peak at 1635 cm^{-1}. Evidently the water molecules are of several sorts and hydrogen bonded. Spectra in both Nujol and KBr disks were essentially identical.

$K_3[Mn(CN)_5NO]$. The spectrum of the anhydrous material has slight but characteristic differences from that of the dihydrate. The NO stretching band is quite broad and appears to consist of two closely overlapping peaks at ~1693 and ~1713 cm^{-1}. The absorptions in the CN stretching region consist of a strong sharp peak at ~2110 cm^{-1} with a weaker peak at ~2135 cm^{-1} and a weak shoulder at 2080 cm^{-1}. The indications that the water in the dihydrate is hydrogen bonded and the changes in the NO stretching absorption on its removal suggest that at least some of the hydrogen bonds are formed to the NO group.

$Zn_3[Mn(CN)_5NO]_2 \cdot xH_2O$. In this salt the characteristic frequencies of the $[Mn(CN)_5NO]^{3-}$ ion are considerably displaced to higher values. The NO stretching band is broad and strong, but relatively symmetrical and occurs at 1800 ± 10 cm^{-1} as compared to about 1700 cm^{-1} in the potassium salt. In the CN stretching region there is a very strong band at ~2145 cm^{-1} and a shoulder at ~2190 cm^{-1}. Thus these frequencies too are shifted up relative to those in the potassium salt. Spectra in Nujol and KBr are essentially identical. Water absorptions are very broad structureless humps centering around 3400 and 1625 cm^{-1}. While the frequency differences between this compound and the potassium salt are unusually large to be attributed to differences in lattice forces there appears to be no other explanation. It may be inferred that not too much significance should be placed on the exact positions of NO stretching bands in attempting to relate their frequencies to the electronic structures of the complex ions in which they occur.

$K_2[Mn(CN)_5NO]$. The spectrum of this compound was taken only in Nujol because of its air-sensitivity. The NO stretching band is very strong and peaks at 1885 ± 5 cm^{-1}. Relatively much weaker peaks were observed at ~2150 and 2100 cm^{-1}, the second of these being considerably weaker than the first. No other bands were observed in the rock salt region.

$Zn[Mn(CN)_5NO]$. As noted in the experimental section this compound reacts with alkali halides and only mull spectra are reliable. The NO stretching band is very strong and peaks at 1885 ± 10 cm^{-1}. Two CN stretching frequencies were observed, the stronger at 2195 cm^{-1} and the weaker at 2150 cm^{-1}.

$Ag_2[Mn(CN)_5NO]$. Like the zinc salt this compound interacts with alkali halides and only mull spectra can be considered reliable. The NO stretching band is very strong and is centered at 1880 ± 10 cm. Only one CN stretching band at ~2175 cm^{-1} was resolved.

Visible and ultra-violet spectra

It is a somewhat curious fact that of the isoelectronic anions $[Fe(CN)_6]^{4-}$, $[Fe(CN)_5CO]^{3-}$, $[Fe(CN)_5NO]^{2-}$ and $[Mn(CN)_5NO]^{3-}$ the first three are pale yellow, yellow-green and red, while the last one is a relatively intense red-purple. In order to see if these striking differences in colour might be due to any fundamental differences in the absorption spectra, the visible and ultra-violet spectra of all these anions were measured using aqueous solutions. The results are summarized in Table 3. Apparently the colour differences result from relatively small variations in band positions and intensities among spectra which are basically similar.

TABLE 3.—VISIBLE AND ULTRA-VIOLET ABSORPTION BANDS

Compound (in aqueous sol'n)	Band position (mμ)	Band position (cm^{-1})	Molar extinction coefficient	Remarks
$K_4[Fe(CN)_6]\cdot 3H_2O$	217	46,100	14,400	
	320	31,200	332	
	498	20,100	1·6	Existence questionable
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	—	—	—	Steeply rising absorption into vacuum UV
	390	35,600	24·6	
	~498	~20,100	~8·9	
$K_3[Fe(CN)_5CO]$	218	45,900	19,000	
	320	31,400	328	
	420	24,100	19·2	
$K_3[Mn(CN)_5NO]$	~220	~45,900	16,400	Very broad; possibly two close bands.
	348	28,600	114	
	540	18,500	23·6	

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