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Disproportionation of Hexacyanomanganate(III) into Hexacyanomanganate(IV) and Hexaquomanganese(II) in Acidic Aqueous Solution

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Hexacyanomanganate(III) hydrolyzes with precipitation of hydrated Mn_2O_3 in pure water but forms rather stable solutions in media as different as alkaline, CN^--containing water or 1 *M* acids [1–5]. UV spectra of these solutions differ markedly [5]. Recently we have shown by comparison with the UV spectra of the solid salts and of solutions in non-aqueous solvents that in CN^--containing water essentially unaffected $Mn(CN)_6^{3-}$ ions are present [6].

We have now extended our study to the acidic solutions of the compounds $M^I_3[Mn(CN)_6]$ (M^I = Na, K). We have employed preparative, analytical and spectroscopic methods in order to trace the species present as well as their manner of formation.

Experimental

Preparations

$K_3[Mn(CN)_6]$ and $Na_3[Mn(CN)_6]\cdot 3H_2O$ were prepared by described procedures [6, 7]. $Cd_3[Mn(CN)_6]_2\cdot 15H_2O$ and $Zn_3[Mn(CN)_6]\cdot 15H_2O$ were obtained by addition of $Na_3[Mn(CN)_6]\cdot 3H_2O$ in small portions to aqueous solutions of an equivalent amount of $CdCl_2$ or $ZnCl_2$ accompanied by vigorous stirring. The light-pink compounds were thoroughly washed with water and dried over P_2O_5 *in vacuo*. *Anal.* $Cd_3[Mn(CN)_6]\cdot 15H_2O$ Calcd.: Cd 32.8, Mn 10.7, N 16.3, C 14.0, H 2.9; found: Cd 32.0, Mn 10.5, N 16.4, C 15.1, H 2.8. $Zn_3[Mn(CN)_6]\cdot 15H_2O$ Calcd.: Zn 22.1, Mn 12.4; found: Zn 21.6, Mn 12.1%.

Experiments to trap $Mn(CN)_6^{2-}$ from acidic solutions of $M^I_3[Mn(CN)_6]$ (M^I = Na, K) were carried out as follows. 100 ml of a 0.05 *M* solution of $M^I_3[Mn(CN)_6]$ in 1 *M* $HClO_4$ were poured into 100 ml of a saturated aqueous $CdCl_2$ or $ZnCl_2$ solution. The yellow precipitates were washed with a little water and dried *in vacuo* over P_2O_5.

Analytical

C, H and N were determined by microanalytical standard methods [8], Mn, Cd and Zn by complexometric titration. Before titration the samples were dissolved in conc. H_2SO_4 and the solution evaporated to dryness to expel the cyanide present. Separation of Zn or Cd from Mn in the prussian blue type salts was achieved by decomposition with diluted NH_3. The complex ion hydrolyzed, forming hydroxidic precipitates of Mn and cyanide, which kept Zn^{2+} and Cd^{2+} in solution. The brown precipitates of Mn were collected on a filter, thoroughly washed and then subjected to iodometric and complexometric titrations. After removal of cyanide Cd^{2+} and Zn^{2+} were determined in the filtrate. The hydrolysis was carried out under N_2 gas to prevent air oxidation of manganese hydroxide to MnO_2. The oxidation number of Mn was established by iodometric titration.

Apparatus

UV spectra of Nujol mulls were measured on a Leitz Unicam SP 800. IR spectra were recorded as Nujol mulls on a Perkin Elmer SP 621.

Results

A first guide to the nature of the species formed in acidic solutions of $M^I_3[Mn(CN)_6]$ (M^I = Na, K) is provided by the UV spectra of these solutions. A striking resemblance to the UV spectrum of $K_2[Mn(CN)_6]$ in DMF previously given by the authors [9] is observed (see Fig. 1). Hexacyanomanganate(III) therefore seems to undergo oxidation to hexacyanomanganate(IV) in acidic solution. Oxygen from air is not an oxidant powerful enough to effect this oxidation nor is direct disproportionation very likely to occur. But on dissolution of $Mn(CN)_6^{3-}$ salts in 1 *M* acids evolution of HCN gas is observed, thus indicating hydrolytic decomposition of at least some part of the cyano complex ions. $Mn(H_2O)_6^{3+}$, the final product of acid hydrolysis of $Mn(CN)_6^{3-}$, should be able to oxidize $Mn(CN)_6^{3-}$ to $Mn(CN)_6^{2-}$. This is reasonable because the standard potential of the

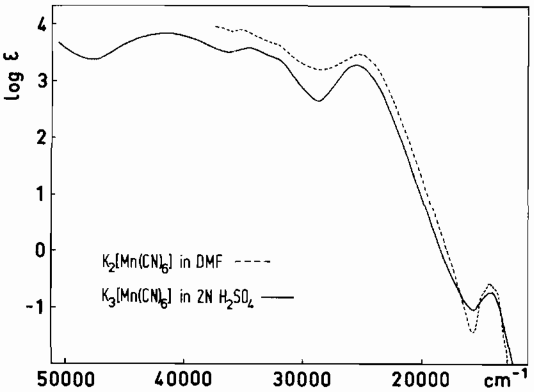

Figure 1. UV spectra of solutions.

TABLE I. Comparison Between the IR Bands of the Prussian Blue Salts Obtained and the Corresponding Potassium Compounds

Assignment	$\nu_{C \equiv N}$		$\delta_{Mn-C \equiv N}$		ν_{Mn-C}	
	Mn(IV)	Mn(III)	Mn(IV)	Mn(III)	Mn(IV)	Mn(III)
Cd salt from acidic solutions of $Na_3[Mn(CN)_6]$	2186 w	2156 m	504 vs	(504)	337 s	388 vw
$Cd_3[Mn(CN)_6]_2 \cdot 15H_2O$		2152 vs		502 m		382 m
Zn salts from acidic solutions of $Na_3[MN(CN)_6]$	2193 w, sh	2163 m	506 vs	(506)	340 s	393 w
$Zn_3[Mn(CN)_6]_2 \cdot 15H_2O$		2160 vs		512 m		390 m
$K_2[Mn(CN)_6]$ [9]	2151 m		484 s		327 s	
$K_3[Mn(CN)_6]$ [6]		2124 2114 vs		481 m		360 s

couple $Mn(H_2O)_6^{2+}/Mn(H_2O)_6^{3+}$ (E_o = 1.52 V) [10] exceeds that of NOCl (E_o^{NO/NO^+} = 1.46 V) [11] serving as oxidant in the preparation of $K_2[Mn(CN)_6]$ [9, 12].

These considerations led us to formulate a hypothetical two-step mechanism describing the disproportionation of $Mn(CN)_6^{3-}$ to $Mn(CN)_6^{2-}$ and $Mn(H_2O)_6^{2+}$ in acidic solution.

$$\text{(I)}\quad Mn(CN)_6^{3-} + 6H_3O^{\oplus} \rightarrow Mn(H_2O)_6^{3+} + 6HCN$$

$$\text{(II)}\quad Mn(CN)_6^{3-} + Mn(H_2O)_6^{3+} \rightarrow Mn(H_2O)_6^{2+} + Mn(CN)_6^{2-}$$

In order to verify this assumption we tried to isolate the species present in acidic solutions and to identify them by analytical and spectroscopic methods.

The average oxidation number of manganese in the acidic solutions is 3.00. That means that in any redox process only manganese itself takes part. A first separation into cationic and anionic species present in these solutions can be achieved by ion exchange. Therefore the solution was passed through a column filled with the H-form of a Lewatit cation-exchange resin type S 1080. In the resulting solution, containing only $H^{\oplus}$ and anions such as the supposed $Mn(CN)_6^{2-}$, the experimentally determined average oxidation number of manganese was 3.80. This confirms the formation of anionic Mn(IV) in acidic solutions of $Mn(CN)_6^{3-}$ salts. When the resin was now treated with 6 N H_2SO_4, Mn^{2+} ions were eluted. Since the exchange resin obviously was not sufficiently stable against oxidation, the ratio of cationic Mn^{2+} to anionic manganese established by complexometric titration was greater than 1.

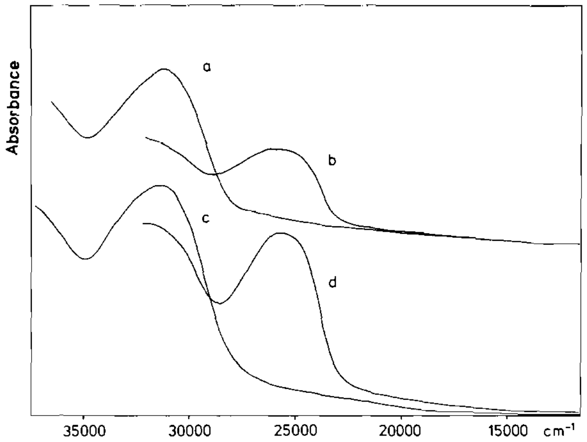

Figure 2. UV spectra of $Cd_3[Mn(CN)_6]_2 \cdot 15H_2O$ (a), $Zn_3[Mn(CN)_6]_2 \cdot 15H_2O$ (c) and of the salts precipitated from acidic solutions of $Na_3[Mn(CN)_6]$ with $CdCl_2$ (b) and $ZnCl_2$ (d) as nujol mulls.

Another method of separating the supposed $Mn(CN)_6^{2-}$ from the simultaneously formed Mn^{2+} involves precipitation of Mn^{2+}. For this purpose $Mn(CN)_6^{3-}$ itself can serve as a counter-ion forming an insoluble prussion blue salt with Mn^{2+}. Thus, if $M_3^I[Mn(CN)_6]$ (M^I = Na, K) is added in portions to an 1 *M* acid at slightly lower temperatures (~10 °C) the initially clear solution soon gets turbid on further addition of $M_3^I[Mn(CN)_6]$ as a result of gradual formation of a solid body. This was removed and identified as $Mn_3[Mn(CN)_6]_2 \cdot 15H_2O$. Obviously, at 10 °C a certain concentration of Mn^{2+} causes competition between formation of $Mn_3[Mn(CN)_6]_2 \cdot 15H_2O$

and hydrolysis of $Mn(CN)_6^{3-}$. Therefore a measurable, though incomplete separation of Mn^{2+} occurs. The average oxidation number of 3.60 for manganese found in the remaining solution reflects the presence of both $Mn(CN)_6^{2-}$ and residual Mn^{2+}.

The reverse mode of procedure involves precipitation of $Mn(CN)_6^{2-}$ by a suitable cation. With divalent metal ions formation of prussian blue salts of the type $M^{II}[Mn(CN)_6]$ could be expected. With the alkaline earths and Ni^{2+} no precipitates were obtained and other ions such as Fe^{2+} and Co^{2+} led to reduction of Mn(IV). But addition of an excess of $CdCl_2$ or $ZnCl_2$ yielded yellow salts exhibiting the same instability and light sensivity as $K_2[Mn(CN)_6]$ [9]. They were characterized analytically and spectroscopically. An average oxidation number of 3.63 and 3.41 for manganese in the Cd and Zn salt respectively has been found. Oxidation to Mn(IV) is thus analytically proven. Possible reasons for its incompleteness are discussed below. UV spectra and IR bands are given in Fig. 2 and Table I. For the sake of comparison spectra of $Cd_3[Mn(CN)_6]_2 \cdot 15H_2O$ and $Zn_3[Mn(CN)_6]_2 \cdot 15H_2O$ are reported as well.

In the UV spectra the band at about 26000 cm^{-1} coincides with the UV absorption of $K_2[Mn(CN)_6]$ at 25500 cm^{-1} [9]. This band is absent in the UV spectra of the $Mn(CN)_6^{3-}$ salts. It is therefore distincitive of $Mn(CN)_6^{2-}$ in the Cd and Zn salts obtained.

In the IR spectra the bands at approximately 2190, 505 and 340 cm^{-1} strongly confirm the presence of $Mn(CN)_6^{2-}$. They can be assigned to $\nu_{C\equiv N}$, $\delta_{Mn-C\equiv N}$ and ν_{Mn-C}. As compared with the potassium salt $K_2[Mn(CN)_6]$ a 30–40 cm^{-1} increase in frequency is observed, which is characteristic of prussian blue salts [13, 14]. Bands at 2160, 510 and 390 cm^{-1} originate from contamination with $Mn(CN)_6^{3-}$ and can be derived from the IR absorptions of $K_3[Mn(CN)_6]$.

Discussion

All our investigations provide clear evidence that formation of $Mn(CN)_6^{2-}$ in acidic solutions of $M^I_3[Mn(CN)_6]$ (M^1 = Na, K) takes place according to the proposed reaction path. But it is remarkable that both in solutions and solids an oxidation number of 4.00 was never reached; a residual contamination with lower valent manganese could not be avoided. This may imply that disproportionation is either incomplete or to some degree reversible or proceeds by a mechanism which is more complex than the one suggested. Some facts point to the reversibility argument. Since the $Mn(CN)_6^{3-}$ coordination polymers are much less soluble than the $Mn(CN)_6^{2-}$ compounds a reversible equilibrium of disproportionation would be shifted to the Mn(III) side for the prussian blue salts. This may account for their low Mn(IV) content. The reasoning also applies to the fact that the Mn(IV) content of the Cd salt is higher than that of the Zn salt, because the $Cd[Mn(CN)_6]$ is less soluble than $Zn[Mn(CN)_6]$.

With Mn^{2+} a pure compound $Mn[Mn(CN)_6]$ can be obtained from acidic solutions of $Mn(CN)_6^{3-}$. The unusual properties of this interesting compound, however, justify its presentation in a separate paper.

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