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The thermal decomposition of metal complexes-V.* The decomposition of some pyridine and substituted-pyridine complexes of manganese (II) halides

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IN PREVIOUS papers of this series details have been given of the preparation and thermal decomposition of complexes formed between pyridine and substituted pyridines and cobalt (II) and nickel (II) halides and between quinoline and a series of metal halides⁽¹⁾ which included manganese (II) halides. This work is now extended to a study of the complexes formed between pyridine and substituted pyridines and manganese (II) halides. The compounds prepared are given in Table 1 together with their temperatures of thermal decomposition and thermal decomposition products. No stoichiometric α -picoline complexes could be prepared. All of the iodide complexes that were isolated contained some free iodine and satisfactory analyses could not be obtained.

TABLE 1.—COMPLEXES FORMED BETWEEN SUBSTITUTED PYRIDINES AND MANGANESE (II) HALIDES AND THEIR THERMAL DECOMPOSITION PRODUCTS

Mnpy₂Cl₂⁽⁶⁾ Mnpy₄Cl₂ MnpyCl₂ Mn, 12.4(12.5); Cl, $16.1(16.1) \xrightarrow{130^{\circ}}$ Mn, 19.4(19.4); Cl, $25.1(25.0) \xrightarrow{340^{\circ}}$ Mn, 26.6(26.8); Cl, 34.0(34.6)Mnapy₂Cl₆ MnCl. $\xrightarrow{270^{\circ}} Mn, 30.2(30.7); Cl, 39.4(39.7) \xrightarrow{250^{\circ}} Mn, 43.2(43.7); Cl, 56.4(56.3)$ $Mn(\beta-pic)Cl_{1}$ $Mn(\beta-pic)_4Cl_2$ $Mn(\beta-pic)_2Cl_1$ Mn, 11·1(11·0); Cl, 14·2(14·2) $\xrightarrow{160^{\circ}}$ Mn, 17·0(17·5); Cl, 22·3(22·6) $\xrightarrow{840^{\circ}}$ Mn, 24·9(25·0); Cl, 31·9(32·3) MnCl₂ $Mn_a(\beta-pic)_2Cl_4$ $\xrightarrow{\text{$270^\circ$}} Mn, 28.7(29.2); Cl, 37.3(37.7) \xrightarrow{\text{50°}} Mn, 43.2(43.7); Cl, 56.2(56.3)$ Mn(y-pic)₄Cl₃ Mn(y-pic)Cl₂ MnCl₂ Mn, 10·9(11·0); Cl, 14·2(14·2) $\xrightarrow{340^{\circ}}$ Mn, 25·1(25·0); Cl, 32·4(32·3) $\xrightarrow{350^{\circ}}$ Mn, 43·0(43·7); Cl, 56·0(56·3) Mn(2·6-lut)Cl₂ MnCl, Mn, 23·7(23·6); Cl, 30·4(30·5) $\xrightarrow{800^{\circ}}$ Mn, 43·7(43·8); Cl, 56·2(56·3) Mn(2·4·6-coll)Cl MnCl, Mn, 21·4(22·2); Cl, 27·9(28·7) $\xrightarrow{860^{\circ}}$ Mn, 42·8(43·8); Cl, 55·9(56·3) Mnpy_sBr₂⁽⁷⁾ Mnpy, Br,⁽⁷⁾ MnpyBr, Mn, 7.7(8.0); Br, 22.6(23.2) $\xrightarrow{140^{\circ}}$ Mn, 14.6(14.7); Br, 42.6(42.9) $\xrightarrow{110^{\circ}}$ Mn, 18.6(18.7); Br, 53.9(54.4) MnBr. ^{s00°}→ Mn, 24·8(25·6); Br, 73·6(74·4) $Mn(\beta-pic)_{1}Br_{1}$ $Mn(\beta-pic)_4Br_1$ $Mn(\beta-pic)Br_1$ Mn, 9·3(9·3); Br, 27·2(27·1) $\xrightarrow{140^{\circ}}$ Mn, 13·7(13·7); Br, 39·7(39·8) $\xrightarrow{s_{10^{\circ}}}$ Mn, 17·7(17·9); Br, 51·4(51·9) $Mn_{a}(\beta-pic)_{a}Br_{6}$ MnBr, $\xrightarrow{\text{360}^{\circ}} \text{Mn}, 19.9(19.8); \text{Br}, 57.4(57.8) \xrightarrow{\text{340}^{\circ}} \text{Mn}, 25.5(25.6); \text{Br}, 74.4(74.4)$ $Mn(\gamma-pic)_{2}Br_{2}$ $Mn(\gamma-pic)_{a}Br_{a}$ Mn(y-pic)Br. Mn, 9·4(9·3); Br, 27·2(27·1) → Mn, 13·6(13·7); Br, 39·9(39·8) → Mn, 17·6(17·9); Br, 52·0(51·9) Mn_a(y-pic)_aBr_a MnBr. $\xrightarrow{380^{\circ}}$ Mn, 19.7(19.8); Br, 57.7(57.8) $\xrightarrow{840^{\circ}}$ Mn, 25.5(25.6); Br, 74.4(74.4)

py = pyridine, pic = picoline(methylpyridine), lut = lutidine(dimethylpyridine), coll = collidine(trimethylpyridine).

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Notes

Previous workers have concluded that the bispyridine-manganese (II) halides have an octahedral environment about the metal atom.^(3,3) X-ray powder photography on the compounds prepared in the present work has shown that $Mn_{a}py_{a}Cl_{e}$ is strictly isomorphous with $Ni_{a}py_{a}Cl_{e}$ and that $MnpyBr_{a}$ is strictly isomorphous with $NipyBr_{a}$ (py = pyridine). The nickel complexes have been shown to have an octahedral environment about the metal and it must be inferred that the two manganese complexes are likewise in octahedral co-ordination. The other complexes are not isomorphous with their nickel analogues but this certainly does not preclude the manganese compounds from having octahedral co-ordination about the metal.

All of the manganese complexes were either white or pale pink in colour and the reflectance spectra are typical of manganese (II) in an octahedral environment. Typical ultra-violet and visible spectra are shown, with their allocations, in Table 2. The $d \rightarrow d$ transitions for a d^5 ion in an octahedral field are all spin forbidden and thus give rise to very weak absorption bands. The charge-transfer bands in the present complexes, particularly the bromides, are intense and many of the $d \rightarrow d$ peaks occur only as shoulders so that no exact measurements can be made of ligand-field relationships. The spectrum of bispyridinemanganese (II) chloride has been recorded previously⁽³⁾ and the present

TABLE 2.---ULTRAVIOLET AND VISIBLE SPECTRA* (All figures are in $m\mu$. The columns correspond to transitions from the ground state ⁶A₁g to the excited states given at the head of the column)

Compound	4T1g(G)	4 T₂g(G)	⁴ Eg(G), ⁴ A ₁ g(G)
$Mn(\beta-pic)_{4}Cl_{2}$	550	470	440
$Mn(\beta-pic)_{2}Cl_{2}$	540	490	425
$Mn(\beta-pic)Cl_{1}$	540	460	420
$Mn_2(\beta-pic)_2Cl_6$	540	460	420
MnCl ₂	540	460	430

* Full details of all of the ultraviolet spectra may be obtained on application to the authors.

measurements are in agreement with that work. The far infra-red spectra of the complexes are again in favour⁽⁴⁾ of octahedral co-ordination about the manganese atoms. In addition to the peaks due to the ligands themselves the chlorides showed a peak near to 235 cm⁻¹ due to a manganese-chloride mode and all of the complexes showed a broad peak near to 230 cm⁻¹ which is associated with a manganese-nitrogen mode. Formulation of the complexes MnL₂X₃, MnLX₃ and Mn₃L₃X₆ (L = substituted pyridine, X = halogen) with octahedral co-ordination about the metal involves polymeric structures with halogen bridging.⁽¹⁾

Previous work on cobalt and nickel has suggested⁽¹⁾ that the complexes of substituted pyridines are generally tetrahedral in compounds of stoichiometry ML_xX_s . The related ligand quinoline brings out tetrahedral co-ordination in iron (II) complexes.⁽⁴⁾ It was hoped therefore that tetrahedral complexes might be observed in the series of manganese complexes but evidently the stabilization of octahedral co-ordination is too great to enable tetrahedral species to be formed.

EXPERIMENTAL

The initial complexes were prepared by refluxing the appropriate halide in the ligand. The resultant complexes were filtered off and washed with ether. References are given in Table 1 where compounds have been reported previously in the literature.

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Notes

All other experimental techniques were carried out in a manner similar to that described in previous parts of this series.

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Hydrolysis of neutron-irradiated uranium and uranium-plutonium monocarbides

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BRADLEY et $al^{(1)}$ have shown that neutron irradiation of uranium monocarbide leads to profound changes in its reactivity with water. We have carried out experiments on the hydrolysis of neutron-irradiated UC and (U, Pu)C which confirm and extend their observations.

Cylindrical specimens of monocarbide (1 in. length, 0.1 in. dia.) were irradiated in the experimental reactor DDO at a maximum thermal neutron flux of $1.8 \times 10^{19} n \text{ cm}^{-3} \text{ sec}^{-1}$ and surface temperatures varying between 550 and 980°C. During irradiation the specimens were in contact with an atmosphere of pure helium. Two years elapsed between removal from the reactor and the execution of the hydrolysis experiments; the latter were performed using conventional equipment, gases being analysed by an "F and M" gas chromatograph with a flame ionization attachment.

The results of hydrolysis with pure water and 4N HCl are summarized in Table 1. A specimen of UC irradiated to 0.4% burn-up (with respect to total heavy atoms) was hydrolysed only slowly in excess water at 80° C, a sample weighing 170 mg taking more than 20 hr to react completely. Specimens irradiated respectively to 0.8 and 1.0% burn-up were completely inert to boiling water, but were hydrolysed readily (15 min) in 4N HCl. None of these irradiated samples of (U, Pu)C tested were attacked by water; hydrolysis by HCl yielded mainly methane and hydrogen. The proportion of hydrogen relative to methane and other volatile hydrocarbons was substantially greater for irradiated than for unirradiated material.

These large changes in chemical reactivity could be ascribed either (i) to a fundamental change in the reactivity of the bulk material brought about by radiation, or (ii) to the influence on hydrolysis of the intense beta radiation field surrounding the irradiated carbide. The second hypothesis was tested by the following experiments. Powdered UC was thoroughly mixed with sufficient ¹⁷⁰Tm₈O₈ to give a beta field approximately equivalent to that of the ⁹⁰Sr which would have accumulated at 1-2% burn-up (100 mg Tm₈O₈/g of UC as fine powder, specific activity 40 mc/g) and the mixture was pressed to small pellets and sintered at 1500°C in argon. A sample of 170 mg of the sintered material was hydrolysed completely in water at 80°C (1 hr), giving essentially the same gaseous products as unirradiated UC.

It seems likely, therefore, that the observed changes in chemical reactivity brought about by irradiation can be ascribed directly to structural changes. Work extending these experiments to material irradiated to higher burn-up ($\sim 10\%$) is in hand.

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