CHEMISTRY LETTERS, pp. 1481-1486, 1974. Published by the Chemical Society of Japan

THERMAL PROPERTIES OF N,N'-DIHYDRO-1,10-PHENANTHROLINIUM AND N,N'-DIHYDRO-2,2'-BIPYRIDINIUM PENTACHLOROMANGANATES(III)

Kozo AKABORI

Department of Chemistry, Faculty of General Education,
Hiroshima University, Higashisenda-machi, Hiroshima 730

The thermal decomposition reactions of $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$ were studied in a flowing atmosphere of nitrogen and in vacuo. These complexes were decomposed thermally in stepwise manners as shown in Table 2. The thermally stable intermediates were isolated easily as their pure forms.

Generally, as to the preparative method of mono-ligand complexes of 1,10-phenanthroline and 2,2'-bipyridine of the type MLX_n, where M is manganese ion, L is phen or bipy and X is halogen, two different procedures are possible: one is to mix the solution of metal halide with organic ligands[1-4], and the another is to heat certain other complexes in furnace and properly to control the course of the reaction.

Recently, the crystal structures of $[H_2(phen)][MnCl_5]$[5] and $[H_2(bipy)][MnCl_5]$[6] have been determined by X-ray diffraction method. These complexes contain the stable structural units N—H---Cl—Mn stabilized by hydrogen bonding.

From these results it can be expected that, since the hydrogen-bonded structures weaken the bond between manganese and chlorine, the complexes of this type involving hydrogen bonds may rather easily liberate an appropriate number of moles of hydrogen chloride to give complexes of the type of $MnLCl_3$, when the compounds are heated under properly controlled conditions. It is thus worthwhile to study the thermal behavior of the complexes $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$ on the basis of this idea. In fact, the mono-ligand complexes of the type MLX_n were isolated in pure forms as the intermediates in the thermally controlled decomposition of $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$, and their

analytical data showed that they are $Mn(phen)Cl_3$, $Mn(bipy)Cl_3$, $Mn(phen)Cl_2$ and $Mn(bipy)Cl_2$. Structures of these intermediates were proposed and determined on the basis of reflectance spectra, X-ray powder diffraction patterns and magnetic moments.

Experimental

Complexes $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$ were prepared by the method of Goodwin and Sylva[3].

DTA-TG measurements were carried out with a Shimadzu Model DTG-2B recording thermal analyzer. Analyses were done in a flowing atmosphere of nitrogen and in vacuo at heating rate of 2°C min^{-1} up to 500°C from room temperature. Finely ground samples (<175 mesh) were used. A constant flow rate of nitrogen of 20 cm^3min^{-1} was used throughout the study. In the case of reduced pressure, the balance housing was then evacuated after air was replaced with nitrogen and kept to a constant pressure of 1×10^{-2}– 2×10^{-2} mmHg during operation of the DTA-TG.

Magnetic susceptibilities of the complexes were measured with a Faraday method over the temperature range of 80-300°K. The magnetic balance was calibrated with Mohr's salt (taking χ_g as $9500\times10^{-6}/(T+1)$ in c.g.s. units). The molar susceptibilities were corrected for diamagnetism, through use of experimental values[7] for chloride, 2,2'-bipyridine and 1,10-phenanthroline.

Results and Discussion

The DTA-TG curves of the complexes $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$ were obtained both in a flowing atmosphere of nitrogen and in vacuo as shown in Fig. 1.

Each of the stable intermediate complexes which we can recognize in this Figure could be obtained in the course of the pyrolysis of the starting complexes $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$ under the conditions shown in Table 1. Reaction schemes of these decompositions, estimated from the temperatures at which each step of reactions is complete and the cumulative percent weight losses in DTA-TG curves, are shown in Table 2.

As shown in Table 2, it is remarkable that both of the trichlorocomplexes cause the electron transfer reaction from the chlorine to the central manganese(III) atom, and change into the manganese(II) complexes, $MLCl_2$. Similar reactions

have been reported in the thermal decomposition studies of Co(III) complexes[8,9].

Two stable complexes, $Mn(phen)Cl_2$ and $Mn(bipy)Cl_2$, in Table 2 were confirmed to be identical with the compounds prepared by Broomhead and Dwyer[1]. X-ray analysis showed that the latter was isomorphous with light-blue $Co(bipy)Cl_2$ obtained by thermal decomposition, and assigned to have an octahedral polymeric structure[10]. Wilde et al. reported also that $Mn(phen)Cl_2$ and $Mn(bipy)Cl_2$ have octahedral polymeric structures[2].

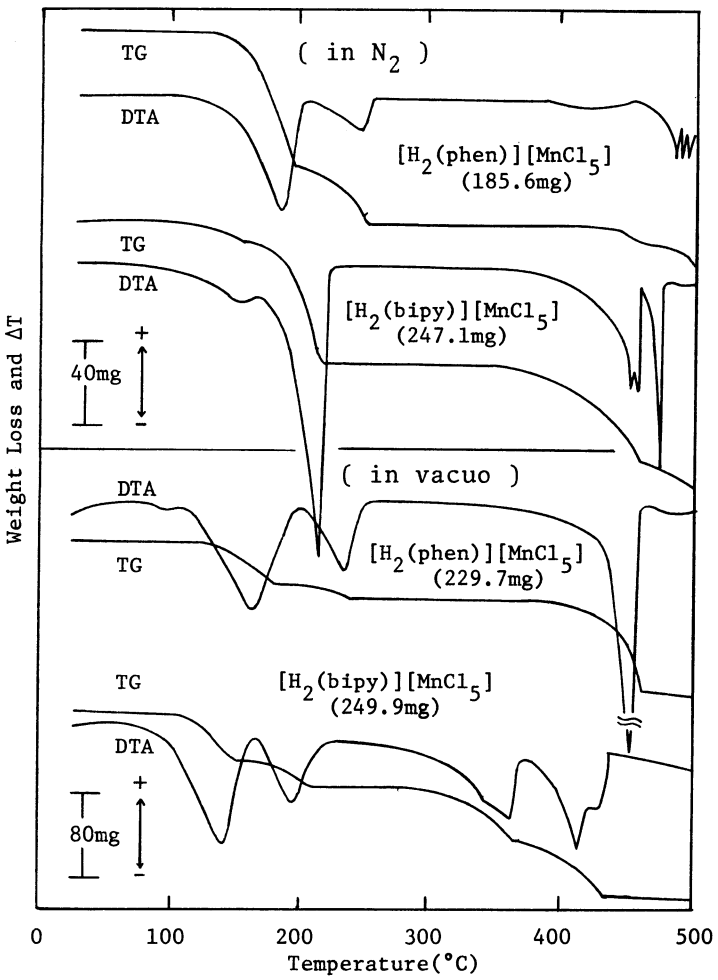

Fig. 1. DTA-TG curves of $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$

From the measurements of reflectance spectra the manganese(III) complexes $Mn(phen)Cl_3$ and $Mn(bipy)Cl_3$ were confirmed to be the compounds reported by Goodwin and Sylva[3], who studied the magnetic properties of these compounds over the temperature range ca. 100-300°K[11]. These two complexes were antiferromagnetics. They concluded that a dimeric or a more highly polymerized octahedral structure is stabilized in them, so that they can show the antiferromagnetic properties either by direct metal-metal interaction or by a super-exchange mechanism through the bridging chlorine atoms. The newly measured magnetic susceptibilities of these compounds at 80-300°K are shown in Fig. 2. All the four complexes appear to follow Curie-Weiss's law. The values of Curie-Weiss constant (Θ) indicate that $Mn(phen)Cl_2$ and $Mn(bipy)Cl_2$ are simply paramagnetic, while $Mn(phen)Cl_3$ and $Mn(bipy)Cl_3$ are antiferromagnetic, as can be expected.

Complexes of divalent manganese are known in both high-spin and low-spin

Table 1. Thermally Stable Intermediate Complexes

Compounds	Elemental analyses (%) C H N Cl	Conditions for isolation
$Mn(phen)Cl_3$	Calc. 42.20 2.36 8.20 31.14 Found 42.46 2.36 8.26 30.96	160°C, 2 hrs., vac.
$Mn(bipy)Cl_3$	Calc. 37.83 2.54 8.82 33.50 Found 38.13 2.55 8.86 33.50	130°C, 2 hrs., vac.
$Mn(phen)Cl_2$	Calc. 47.09 2.63 9.15 23.17 Found 46.69 2.48 9.08 24.06	233°C, 2 hrs., vac.
$Mn(bipy)Cl_2$	Calc. 42.59 2.86 9.93 25.14 Found 42.30 2.70 9.78 25.32	198°C, 3 hrs., vac.

Table 2. Reaction Schemes of $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$

(in nitrogen atmosphere)

$$[H_2(phen)][MnCl_5] \xrightarrow[17.4(17.6\%)*]{-2HCl,\ 197°C} Mn(phen)Cl_3 \xrightarrow[24.4(26.2\%)]{-0.5Cl_2,252°C} Mn(phen)Cl_2$$

$$[H_2(bipy)][MnCl_5] \xrightarrow[27.1(27.8\%)]{-(2HCl+0.5Cl_2),217°C} Mn(bipy)Cl_2 \xrightarrow[44.5(47.8\%)]{-0.5bipy,462°C} Mn(bipy)_{0.5}Cl_2$$

(in vacuo)

$$[H_2(phen)][MnCl_5] \xrightarrow[17.7(17.6\%)]{-2HCl,185°C} Mn(phen)Cl_3 \xrightarrow[25.4(26.2\%)]{-0.5Cl_2,245°C} Mn(phen)Cl_2 \xrightarrow[67.9(69.6\%)]{-phen,460°C} MnCl_2$$

$$[H_2(bipy)][MnCl_5] \xrightarrow[18.8(18.7\%)]{-2HCl,155°C} Mn(bipy)Cl_3 \xrightarrow[27.8(27.8\%)]{-0.5Cl_2,215°C} Mn(bipy)Cl_2 \xrightarrow[48.2(47.8\%)]{-0.5bipy,365°C}$$

$$\rightarrow Mn(bipy)_{0.5}Cl_2 \xrightarrow[68.6(67.8\%)]{-0.5bipy,437°C} MnCl_2$$

(* Parentheses indicate the theoretical cumulative percent weight loss for the indicated loss)

forms. The high-spin complexes are expected to show magnetic moments very close to the spin-only value (5.92 B.M.) and independent of temperature. In Fig. 2, $Mn(phen)Cl_2$ and $Mn(bipy)Cl_2$ show these behaviors: the former; μ_{eff}, 5.80 B.M. at 105.5°K and 5.88 B.M. at 299.2°K. the latter; μ_{eff}, 5.85 B.M. at 105.0°K and 5.81 B.M. at 296.0°K.

For the octahedral, high-spin d^4 complexes, the magnetic moment is expected to be the spin-only value modified by the factor $(1-2\lambda/10Dq)$ and to be independent of temperature[12]. For a low-spin complexes, magnetic moment has a complicated

dependence with temperature[12]. The moment at room temperature should be approximately 3.5 B.M. and should fall rapidly with the decrease of temperature[12]. The moments of $Mn(phen)Cl_3$ and $Mn(bipy)Cl_3$ show, in fact, complicated temperature dependence, but their magnetic behaviors were more peculiar: the former; μ_{eff}, 2.85 B.M. at 81.2°K and 4.26 B.M. at 299.4°K. the latter; μ_{eff}, 2.85 B.M. at 81.2°K and 4.27 B.M. at 299.1°K. These temperature dependences were similar to those of the complexes obtained by Goodwin and Sylva.

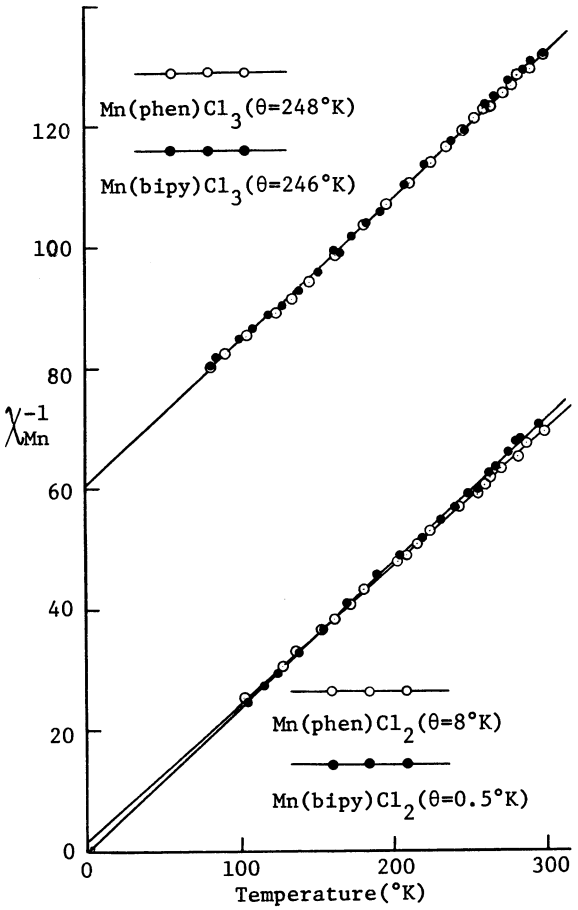

Fig. 2. Inverse of molar susceptibility vs. temperature.

Conclusion

The obtained results thus show that the thermally stable complexes of the type MLX_n can be synthesized by the method of the pyrolysis of the complexes involving hydrogen bonds, i.e., $[H_2(phen)][MnCl_5]$ and $[H_2(bipy)][MnCl_5]$. The isolated complexes are $Mn(phen)Cl_3$, $Mn(bipy)Cl_3$, $Mn(phen)Cl_2$ and $Mn(bipy)Cl_2$. $Mn(phen)Cl_2$ and $Mn(bipy)Cl_2$ are simply paramagnetic, while $Mn(phen)Cl_3$ and $Mn(bipy)Cl_3$ are antiferromagnetic. These intermediate complexes are supposed to have octahedral stereochemistries.

References

1) J. A. Broomhead and F. P. Dwyer, Aust. J. Chem., 14, 250 (1961).
2) R. E. Wilde, T. K. K. Srinivasan, and S. N. Ghosh, J. Inorg. Nucl. Chem., 35, 1017 (1973).
3) H. A. Goodwin and R. N. Sylva, Aust. J. Chem., 18, 1743 (1965).
4) H. Funk and H. Kreis, Z. Anorg. Chem., 349, 45 (1967).
5) M. Matsui, S. Koda, S. Ooi, H. Kuroya, and I. Bernal, Chem. Lett., 51 (1972).
6) I. Bernal, N. Elliott, and R. Lalancette, Chem. Commun., 803 (1971).

7) A. Earnshaw, "Introduction to MAGNETOCHEMISTRY", Academic Press, London and New York (1968), p. 5.

8) N. Tanaka and M. Nanjo, Bull. Chem. Soc. Japan, 37, 1330 (1964).

9) W. W. Wendlandt and E. L. Simmons, J. Inorg. Nucl. Chem., 27, 2317 (1965).

10) K. Akabori, H. Matsuo, and Y. Yamamoto, J. Inorg. Nucl. Chem., 33, 2593 (1971).

11) H. A. Goodwin and R. N. Sylva, Aust. J. Chem., 20, 629 (1967).

12) B. N. Figgis and J. Lewis, "Progress in Inorganic Chemistry" (F. A. Cotton, ed.), Interscience, New York (1964), 6, p. 37.

(Received October 7, 1974)