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## Note

# Metal perchlorate ammines: thermal and infrared studies

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While studying the catalytic effect of transition metal perchlorate ammines on the thermal decomposition of ammonium perchlorate[1], the ignition characteristics of pure metal perchlorate ammines gave interesting results. On looking through the literature it was found that, whereas preparation and explosive properties of the metal perchlorate ammines have been described[2–6], no detailed account of the nature of intermediates and products of decomposition of these metal perchlorate ammines are reported. In the present study we report, the preparation, infrared spectra and the thermal decomposition characteristics of some of the transition metal perchlorate ammines and their intermediates.

## EXPERIMENTAL

The metal perchlorate hexahydrates were prepared by the reaction of metal carbonates, oxides or hydroxides with 60% perchloric acid and the perchlorate salts were crystallised from water and washed with chloroform. The metal perchlorate ammines were prepared as reported earlier[2,3], by refluxing ~2 g of the freshly prepared hexahydrate with ~25 ml of anhydrous liquid ammonia. The details of the experimental set-up are described elsewhere[7]. Differential thermal analysis (DTA) and thermogravimetry (TG) units employed were similar to those described earlier[8]. All experiments were done in air. Heating rates employed were 12 °C $min^{-1}$ for DTA and 5 °C $min^{-1}$ in the case of TG. Platinum cups were used as sample holders in DTA experiments. Since the metal perchlorate ammines are highly explosive the amount of the sample used was restricted to $<30$ mg. Infrared spectra were recorded on a Carl-Zeiss Jena UR-10 double beam infrared spectrophotometer using KBr pellets as well as Nujol mulls.

## RESULTS AND DISCUSSION

The results of thermal analyses of metal perchlorate ammines are presented in Table 1. All the complexes decompose in two steps as observed by Sherrif and

TABLE 1

THERMAL DECOMPOSITION DATA OF METAL PERCHLORATE AMMINES

| $[M(NH_3)_6](ClO_4)_2$ | DTA peak temp. (°C) | Thermogravimetry |  | Reaction |
|---|---|---|---|---|
| M |  | % weight loss |  |  |
|  |  | Obsd. | Cal. |  |
| Mn | 93 (Endo) | 19.0 | 19.11 | Eqn (1) |
|  | 234 (Exo) | — | — | Eqn (2) |
| Co | 122 (Endo) | 18.78 | 18.89 | Eqn (1) |
|  | 222 (Exo) | — | — | Eqn (2) |
| Ni | 110 (Endo) | 18.55 | 18.9 | Eqn (1) |
|  | 240 (Exo) | — | — | Eqn (2) |
| Cu | 122 (Endo) | 9.30 | 9.33 | Eqn (1) |
|  | 222 (Exo) | — | — | Eqn (2) |
| Zn | 80 (Endo) | 9.25 | 9.28 | Eqn (1) |
|  | 330 (Exo) | — | — | Eqn (2) |
| Cd | 90 (Endo) | 16.45 | 16.45 | Eqn (1) |
|  | 307 (Exo) | — | — | Eqn (2) |

Galway[6] for nickel perchlorate hexaammine. The formation of completely deammoniated metal perchlorate was not observed in any case.

$$[M(NH_3)_6](ClO_4)_2 \xrightarrow{\sim 100\,^\circ C} [M(NH_3)_x](ClO_4)_2 + (6-x)NH_3 \qquad (1)$$

$x = 2$, for M = Mn, Co, Ni and Cd;

$x = 4$, for M = Cu and Zn.

$$[M(NH_3)_x](ClO_4)_2 \xrightarrow{>220\,^\circ C} \text{explodes} \qquad (2)$$

The intermediate decomposition product is the di-ammine in most cases and tetra-ammine in the case of copper and zinc. The composition of the intermediate ammines was fixed by the observed weight-loss in TG (Table 1). These intermediate ammines decompose explosively to their respective metal oxides and not to metal chlorides as reported earlier[4]. Only cadmium perchlorate di-ammine decomposes to give cadmium chloride. The formation of the metal oxide was indicated by the insolubility of the residue, its color and negative test for $Cl^-$ ions. No TG estimation of the residue was possible because of the explosive reaction. Wendlandt and co-workers have also observed the formation of oxide rather than chloride in the study of thermal decomposition of the cobalt and copper nitrate ammines[9,10].

The observed infrared absorption frequencies of metal perchlorate hexaammines and the intermediate ammines are presented in Table 2. The assignments of

TABLE 2

INFRARED ABSORPTION FREQUENCIES OF METAL PERCHLORATE AMMINES (cm$^{-1}$)

M = Mn, Co, Ni, Cu, Zn and Cd, $x = 2$ for Mn, Co, Ni and Cd and $x = 4$ for Cu and Zn.

| | $[M(NH_3)_6](ClO_4)_2$ | $[M(NH_3)_x](ClO_4)_2$ |
|---|---|---|
| *Ammonia bands* | | |
| $\nu(NH_3)_{asym.}$ | 3400 | 3300 |
| $\nu(NH_3)_{sym.}$ | 3300 | |
| $\delta_d(NH_3)$ | 1620 | 1620 |
| $\delta_s(NH_3)$ | 1240–1270 | 1400–1410 |
| $\rho_r(NH_3)$ | 750 | 750 |
| $\nu_{M-N}$ | 420–450 | 420–450 |
| *Perchlorate bands* | | |
| $\nu_3$ | 1100 | 1210, 1150, 1100<br>(1150, 1125, 1095)[a] |
| $\nu_1$ | 940 | 940 |
| $\nu_4$ | 630 | 635, 630 |

[a] Bands observed in the case of M = Cu and Zn.

the characteristic absorption frequencies of the coordinated ammonia are similar to those of Nakamoto[11]. The observed absorption bands ~1100 ($\nu_3$), 940 ($\nu_1$) and 630 ($\nu_4$) cm$^{-1}$ in the case of hexa-ammines indicate the presence of simple perchlorate ion having $T_d$ symmetry in these complexes. The infrared absorption frequencies of the intermediate ammines, however, show a marked difference. The infrared frequencies of these ammines show appreciable splitting in the $\nu_3$ and $\nu_4$ region of the perchlorate group. The splittings can be explained to be due to the presence of mono- or bi-dentate perchlorate group coordinating to the metal ion, changing the $T_d$ symmetry of the perchlorate group to $C_{3v}$ or $C_{2v}$ similar to those observed in the case of metal perchlorate dihydrates[12,13]. The difference in the infrared spectra of the hexa- and the intermediate ammines could be visualized to be due to the migration of the $ClO_4$ groups in the vacancies created by the loss of ammonia molecules.

A close inspection of the infrared data of the intermediate ammines appears to indicate the presence of H-bonding in these molecules. As can be seen from Table 2, the N–H stretching frequency of these intermediate ammines appears as a single broad band ~3300 cm$^{-1}$. Further, the $NH_3$ deformation band which appears ~1250 cm$^{-1}$ in the hexa-ammines appears to be shifted to ~1400 cm$^{-1}$ in the intermediate ammines. Both these observations may be attributed to the presence of H-bonding[11] between the N–H proton and oxygen atom of the $ClO_4$ group. The H-bonding appears to be responsible for holding the ammonia molecules in the intermediate ammines. This probably explains why it is not possible to deammoniate completely these intermediate ammines to yield pure metal perchlorates, prior to decomposition.

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