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THE THERMAL DEAQUATION OF SOME COBALT(II) SALT HYDRATES

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ABSTRACT

The solid-state thermal deaquation reactions of the compounds, $CoX_2 \cdot 6H_2O$ ($X = Cl$, Br, NO_3), $CoSO_4 \cdot 7H_2O$, and $Co(OAc)_2 \cdot 4H_2O$, were investigated by thermogravimetry, DTA, magnetic susceptibility and electrical conductivity techniques. Quantitative DTA measurements were made to determine the reaction enthalpies using both sealed and open sample containers. The effects of the presence of water vapor on the deaquation reactions were also studied.

INTRODUCTION

The thermal deaquation reactions of the cobalt(II) salt hydrates have been extensively investigated. It is apparent from these investigations that the nature of the anions in the outer coordination sphere strongly influences the ease of dehydration and the type of intermediate species produced. Regardless of the nature of the outer sphere ions, however, the cobalt(II) salt hydrates each exist in the liquid phase between 50 and 150°C. The exact nature of the species present in this liquid phase has never been elucidated.

The chloride, $CoCl_2 \cdot 6H_2O$, has been extensively studied by thermogravimetry, reflectance spectroscopy, X-ray diffraction, and DTA[1-11]. Stable 1- and 2-hydrates were found as reaction intermediates during the thermal deaquation. Thermogravimetric and X-ray diffraction studies indicated that the corresponding bromide, $CoBr_2 \cdot 6H_2O$, formed 5-, 4-, 2- and 1-hydrate intermediates[12] and possibly 5.5- and 0.5-hydrates as well[13]. The compound, $CoBr_2 \cdot 5H_2O$, has been prepared by careful deaquation of the 6-hydrate[14]. Reflectance studies[11] revealed a strong increase in the absorption of light in the visible regions after the phase transition at about 50°C for both the chloride and the bromide compounds. The increases were thought to be due to the presence of tetrahedral cobalt(II) species in the liquid phase.

The sulfate, $CoSO_4 \cdot 7H_2O$, has been found to lose six moles of water in a single step at about 100°C indicating that one mole of water is bonded differently[15-22]. In fact, it has been shown that the correct formula for the 1-hydrate is CoH_2SO_5[23,24]. The final water molecule is lost above 300°C.

The deaquation of the nitrate, $Co(NO_3)_2 \cdot 6H_2O$, has been studied at both high[25] and low temperatures[26–28]. It is possible, apparently, to prepare the 5-, 4-, 3-, and 2-hydrates. The perchlorate, $Co(ClO_4)_2 \cdot 6H_2O$, forms the 4- and 2-hydrate intermediates during the thermal deaquation reactions[29].

The acetate is unusual in that it is usually obtained as the 4-hydrate, $Co(OAc)_2 \cdot 4H_2O$, and it forms a series of basic cobalt(II) acetates during the subsequent thermal decomposition reactions[30–32]. Other cobalt(II) salt hydrates whose thermal deaquation reactions have been investigated include the formate[33], phosphate,[34,35] bromate[36], fluoride[37], iodide[38], and cyanide[39] compounds. Again, the ease of deaquation and the nature of the reaction intermediates depended on the nature of the anion present.

In this investigation, the thermal deaquation reactions of the compounds, $CoX_2 \cdot 6H_2O$ ($X = Cl$, Br, NO_3, ClO_4), $CoSO_4 \cdot 7H_2O$, and $Co(OAc)_2 \cdot 4H_2O$, were further investigated by thermogravimetry and DTA as well as by magnetic susceptibility and electrical conductivity. The heats of the reactions were determined by quantitative DTA using both sealed and open tube sample containers. The effects of water on the thermal deaquation reactions were also studied.

EXPERIMENTAL PART

Materials

The compounds used in this investigation were all of analytical reagent grade quality.

Thermogravimetry

The thermogravimetric studies were carried out by the use of a DuPont 950 thermogravimetric analyzer. From 3–6 mg samples were used and the heating rate was 2.5, 5, or 10°C/min. The dynamic furnace atmosphere was either dry or water saturated nitrogen.

DTA

The DTA curves of the compounds were obtained on an apparatus previously described[44]. Samples were placed in sealed or open capillary tubes, each 1.6–1.8 mm I.D. A heating rate of 5°C/min was employed. The quantitative DTA data were obtained as previously described[44].

Magnetic susceptibility

The magnetic susceptibilities of the compounds from ambient room temperature to 100°C were obtained by the Faraday method. The heating rate was 10°C/min while the sample masses ranged from 0.5–3 mg.

Electrical conductivity

The electrical conductivity curves were obtained on the apparatus previously described[45]. A heating rate of 5°C/min was employed for all measurements.

RESULTS AND DISCUSSION

TG results

The TG curves of $CoCl_2 \cdot 6H_2O$ in dry and water saturated nitrogen atmospheres and for three different heating rates are shown in Fig. 1. In each case, three mass-losses were observed. The intermediate hydrates, $CoCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot H_2O$, were observed while the final product was $CoCl_2$. The minimum temperatures at which each mass-loss occurred was increased by the presence of water in the furnace atmosphere. The existence of a reaction intermediate was also more clearly defined on the TG curves if water was present in the atmosphere. As expected, the minimum temperatures at which each mass-loss occurred increased with increasing heating rate.

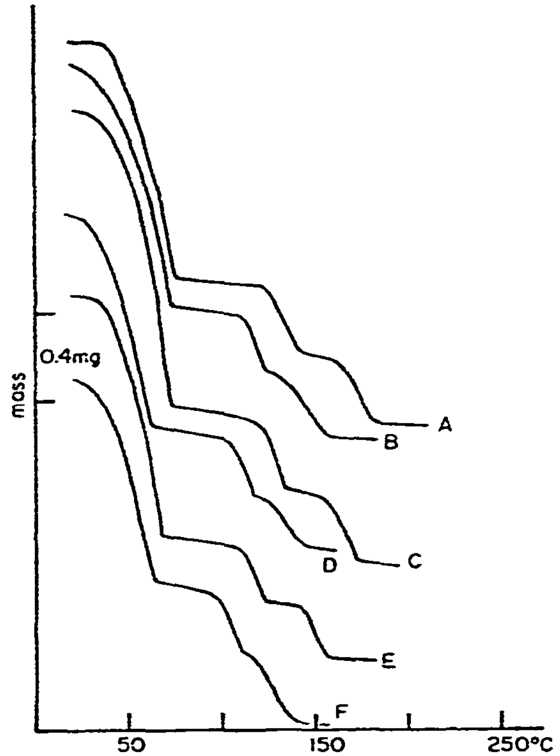

Fig. 1. TG curves of $CoCl_2 \cdot 6H_2O$. A, 10°C/min, H_2O satd. N_2; B, 10°C/min, dry N_2; C, 5°C/min, H_2O satd. N_2; D, 5°C/min, dry N_2; E, 2.5°C/min, H_2O satd. N_2; F, 2.5°C/min, dry N_2.

The TG curves for $CoBr_2 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ in both a dry and a water saturated atmosphere are illustrated in Fig. 2. The curves for the bromide do not reveal the presence of intermediate hydrates as clearly as those for the chloride. Small breaks in the curves, however, indicated the possible formation of the 4-hydrate. The sulfate lost six coordinated water molecules to form the 1-hydrate. No other intermediates were evident. Again, the reaction temperatures were increased by the presence of water vapor in the furnace atmosphere.

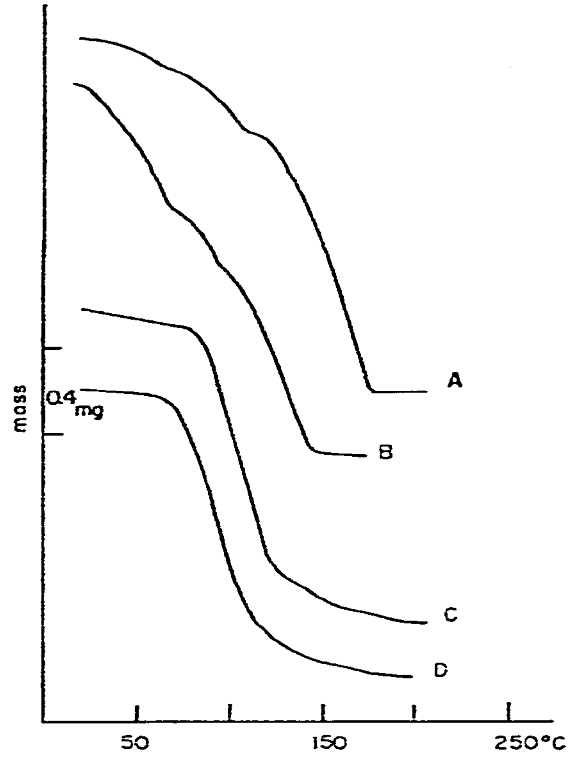

Fig. 2. TG curves of cobalt(II) salt hydrates at 5°C/min. A, $CoBr_2 \cdot 6H_2O$, H_2O satd. N_2; B, $CoBr_2 \cdot 6H_2O$, dry N_2; C, $CoSO_4 \cdot 7H_2O$, H_2O satd. N_2; D, $CoSO_4 \cdot 7H_2O$, dry N_2.

The TG curves for $Co(ClO_4)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Co(OAc)_2 \cdot 4H_2O$ are illustrated in Fig. 3. The perchlorate formed the 4-hydrate intermediate in an atmosphere saturated with water vapor but formed the 2-hydrate intermediate in a dry nitrogen atmosphere. These were the only reaction intermediates observed and both hydrates have previously been obtained[29]. The last mass-loss in both cases corresponded to the decomposition to cobalt oxide.

The TG curves for the compound, $Co(NO_3)_2 \cdot 6H_2O$, indicated the formation of four intermediate compounds, the 5-, 3-, and 1-hydrates, and anhydrous cobalt(II) nitrate. Each of these hydrates has previously been prepared as have the 4- and 2-hydrates. The latter two hydrates were not evident in the curves. The presence of the reaction intermediates were much more clearly defined in the TG curve obtained with a water saturated atmosphere than that in a dry nitrogen atmosphere.

The TG curves for the compound, $Co(OAc)_2 \cdot 4H_2O$, are especially unusual. The presence of water vapor in the furnace atmosphere completely altered the course of the reaction. In both a dry and a water saturated atmosphere the first mass-loss apparently corresponded to the previously observed[31] loss of two moles of water to form the 2-hydrate. The second mass-loss at about 75°C, in both cases, corresponded to the formation of the basic acetate, $Co_4(OAc)_7OH \cdot 2H_2O$, which has also been reported[31]. In a water saturated atmosphere, the basic acetate intermediate decomposed in a single step at 225 °C while in a dry nitrogen atmosphere, another reaction intermediate was formed at that temperature. This intermediate, which is probably the previously observed compound, $Co_3(OAc)_5OH$, decomposed at about 280 °C[31].

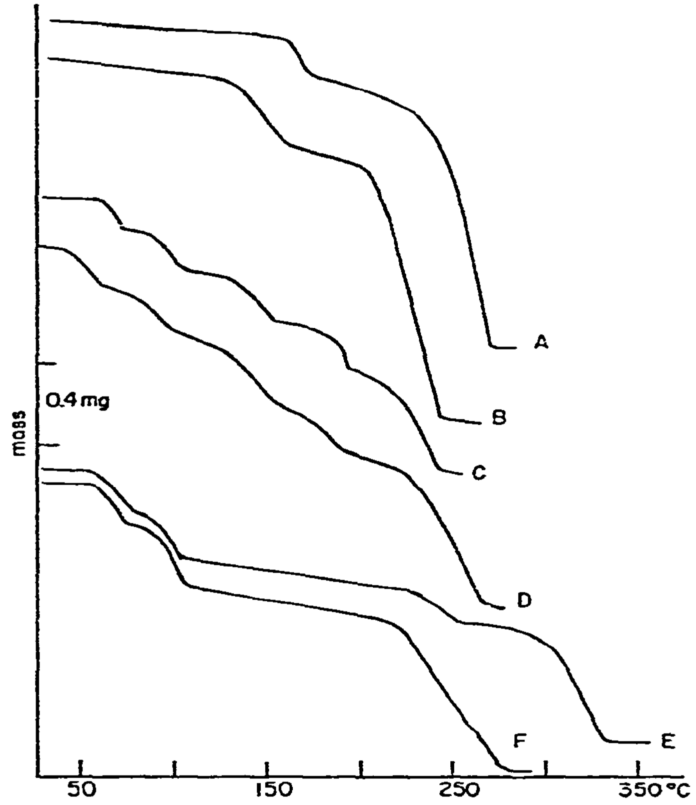

Fig. 3. TG curves of cobalt(II) salt hydrates at 5 °C/min. A, $Co(ClO_4)_2 \cdot 6H_2O$, H_2O satd. N_2; B· $Co(ClO_4)_2 \cdot 6H_2O$, dry N_2; C, $Co(NO_3)_2 \cdot 6H_2O$, H_2O satd. N_2; D, $Co(NO_3)_2 \cdot 6H_2O$, dry N_2; E, $Co(OAc)_2 \cdot 4H_2O$, dry N_2; F, $Co(OAc)_2 \cdot 4H_2O$, H_2O satd. N_2.

DTA curves

The DTA curves for $CoCl_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$, and $CoSO_4 \cdot 7H_2O$ are illustrated in Fig. 4, while those for $Co(NO_3)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, and $Co(OAc)_2 \cdot 4H_2O$ are illustrated in Fig. 5. For each compound an endothermic reaction was observed at about 50–60 °C. This reaction corresponded to the phase transition, *solid → liquid*. The other three endothermic peaks in the curve for $CoCl_2 \cdot 6H_2O$ corresponded to the loss of four moles of water at about 125 °C and the loss of the remaining water at 175 and 225 °C, respectively. The DTA curve for $CoBr_2 \cdot 6H_2O$ is almost identical to that observed for the chloride and each peak undoubtedly corresponds to the same type of reaction, although these reactions were not so apparent on the corresponding TG curve.

The large endothermic peak in the DTA curve for $CoSO_4 \cdot 7H_2O$ at about 125 °C was due to the loss of all six moles of water. Although several intermediate hydrates appear on the TG curve of $Co(NO_3)_2 \cdot 6H_2O$, the evolution of all six moles of water occurred as one broad endothermic peak in the DTA curve. For the perchlorate, the first deaquation reaction appears on the DTA curve as a very small endothermic peak while the deaquation reaction appears as a larger endothermic peak at just over 200°C. The DTA curve for the acetate clearly reveals three endothermic reactions other than the phase transition at about 60°C. These apparently correspond to the three mass losses revealed on the TG curve for the reaction in a water saturated atmosphere. The temperature for the final reaction, however, is lower on the DTA curve than on the TG curve. This is probably due to the higher concentration of water vapor present in the DTA sample tubes. The same phenomenon is probably responsible for the apparently higher temperature for all of the deaquation reactions revealed by the DTA curves.

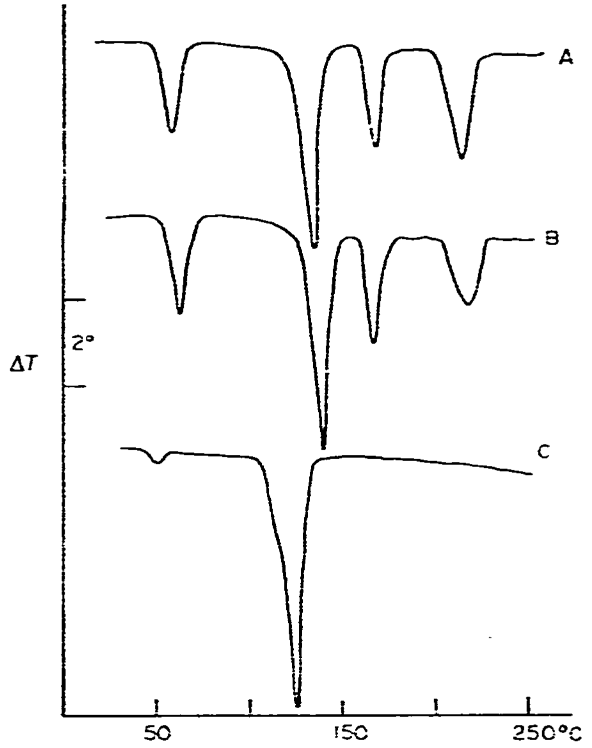

Fig. 4. DTA curves of cobalt(II) salt hydrates. A, $CoCl_2 \cdot 6H_2O$; B, $CoBr_2 \cdot 6H_2O$; C, $CoSO_4 \cdot 7H_2O$.

Table I gives the heats of the phase transitions, ΔH_t, for $CoCl_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ in the 50–60°C temperature range as obtained by quantitative DTA measurements, using both open and a sealed reaction tubes. There was little difference between the values obtained by the two methods indicating that the reaction is a phase transition only (no vaporization energy is involved). The order of decreasing heats of transition was: Cl> Br> NO_3.

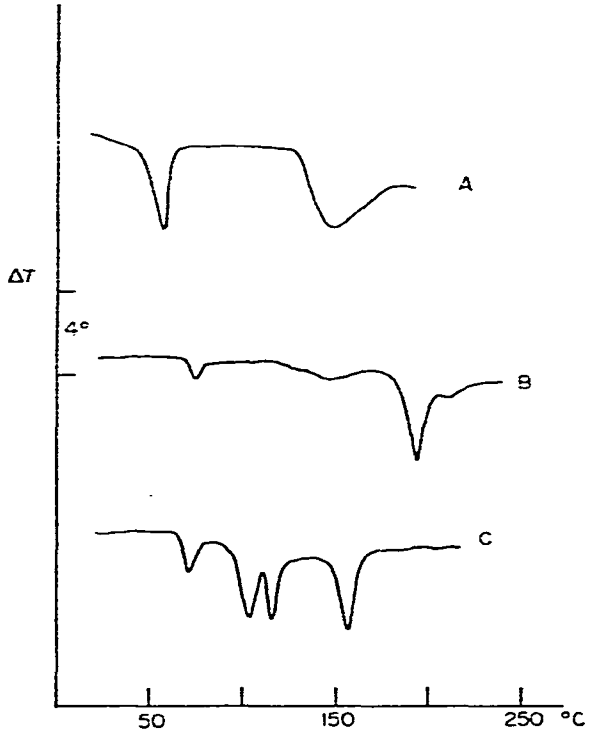

Fig. 5. DTA curves of cobalt(II) salt hydrates. A, $Co(NO_3)_2 \cdot 6H_2O$; B, $Co(ClO_4)_2 \cdot 6H_2O$; C, $Co(OAc)_2 \cdot 4H_2O$.

TABLE I

HEATS OF THE *solid→liquid* PHASE TRANSITION OF THE COBALT(II) SALT HYDRATES

Compound	*ΔH_t, open tube (kcal/mole)*	*ΔH_t, sealed tube (kcal/mole)*
$CoCl_2 \cdot 6H_2O$	12.4	12.3
$CoBr_2 \cdot 6H_2O$	11.9	11.8
$Co(NO_3)_2 \cdot 6H_2O$	11.0	10.7

Magnetic susceptibility measurements

Curie–Weiss plots for the compounds, $CoX_2 \cdot 6H_2O$ ($X = Cl$, Br, NO_3, ClO_4) and $Co(OAc)_2 \cdot 4H_2O$, are illustrated in Figs. 6 and 7. As can be seen, sharp deviations in the linear curves occurred at the temperature of the phase transitions for the chloride, bromide, and nitrate. The deviation was largest for the chloride and smallest for the nitrate. No deviation from linearity was detected in the curves for the perchlorate and the acetate; they were linear up to 100 °C. The effective magnetic moment, μ_{eff}, for each of the compounds corresponded to that for an octahedral cobalt(II) complex both before and *after* the phase transition. The values of μ_{eff} for the five compounds are listed in Table II.

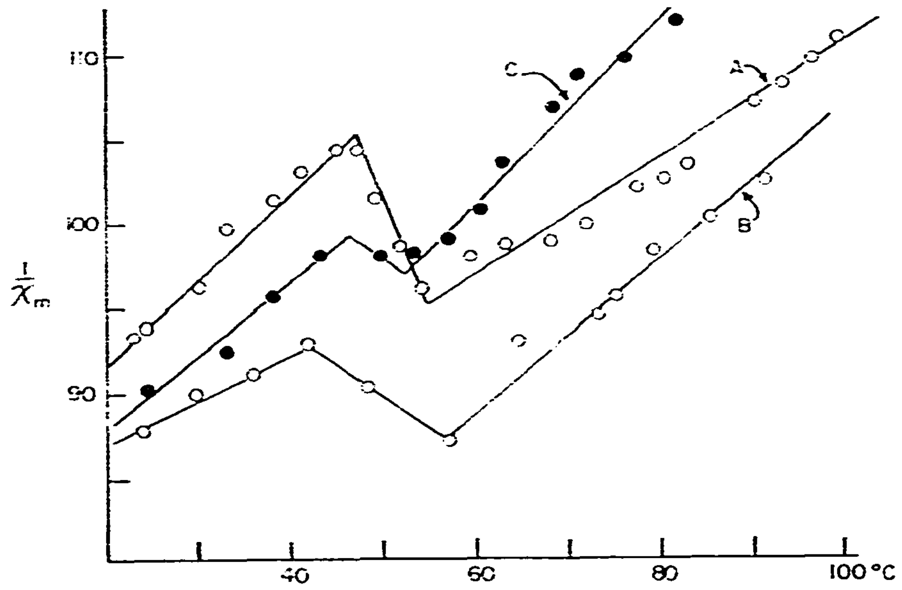

Fig. 6. Curie–Weiss plots of cobalt(II) compounds. A, $CoCl_2 \cdot 6H_2O$; B, $CoBr_2 \cdot 6H_2O$; C, $Co(NO_3)_2 \cdot 6H_2O$.

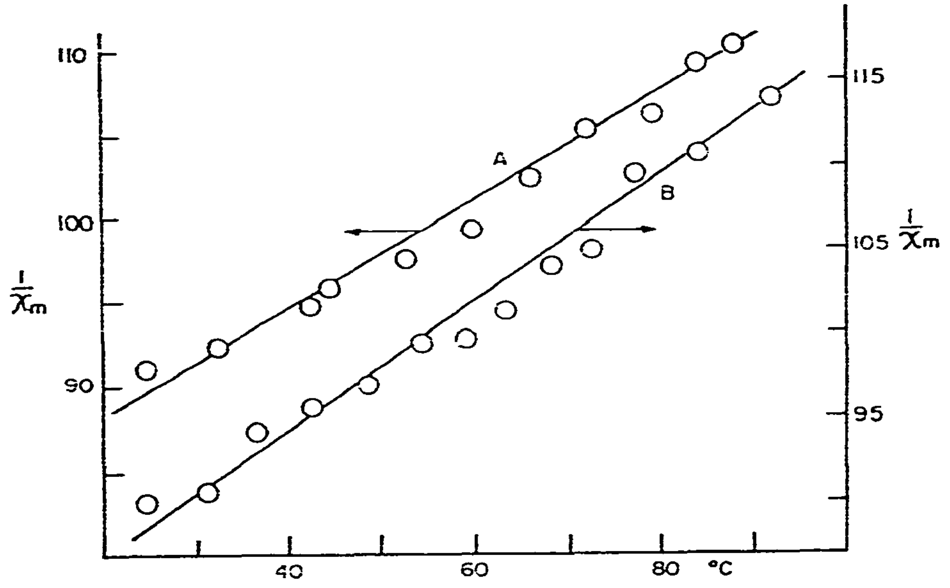

Fig. 7. Curie–Weiss plots of cobalt(II) compounds. A, $Co(OAc)_2 \cdot 4H_2O$; B, $Co(ClO_4)_2 \cdot 6H_2O$.

Electrical conductivity

The electrical conductivity curves for $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6H_2O$ are shown in Fig. 8. As can be seen, there was a large increase in the electrical conductivity between 50 and 140°C for the chloride, and between 50 and 160°C for the bromide. This indicates that these are the temperature ranges at which the compounds are in the liquid state and conduction is by the ionic species that are present.

TABLE II

EFFECTIVE MAGNETIC MOMENTS OF COBALT(II) COMPOUNDS

Compound	*μ_{eff}(B.M.)*	
	25°C	*60°C*
$CoCl_2 \cdot 6H_2O$	5.06	5.25
$CoBr_2 \cdot 6H_2O$	5.23	5.40
$Co(NO_3)_2 \cdot 6H_2O$	5.14	5.14
$Co(ClO_4)_2 \cdot 6H_2O$	5.13	
$Co(OAc)_2 \cdot 4H_2O$	5.14	

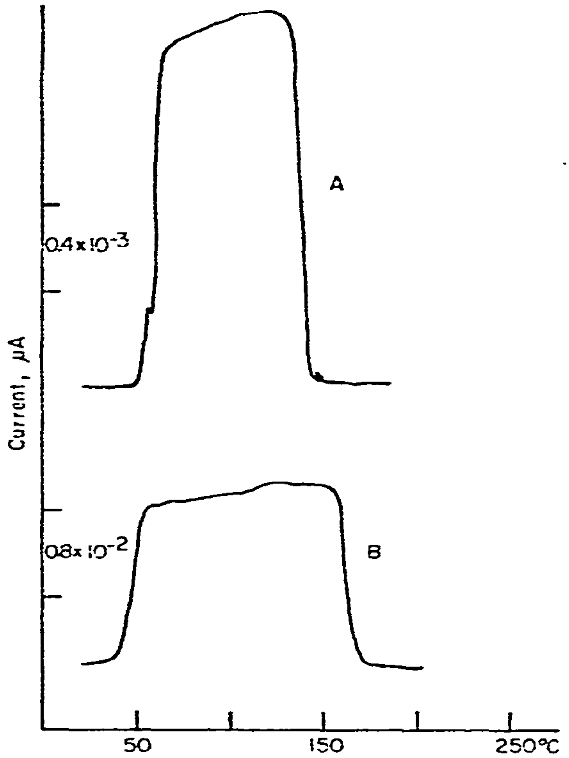

Fig. 8. Electrical conductivity curves of several cobalt(II) compounds. A, $CoCl_2 \cdot 6H_2O$; B, $CoBr_2 \cdot 6H_2O$.

General

The manner in which the outer sphere anions of the cobalt(II) salt hydrates affect the thermal deaquation reactions and the nature of the reaction intermediates is obviously quite complicated. Perhaps the major factors involved are the size, the charge, the complexity and the ligand field strengths of the anions. For example, during the *solid → liquid* phase transition at about 50°C, the magnitude of the change from linearity in the Curie–Weiss plot decreases in the order: $Cl > Br > NO_3$.

This is also the order of decreasing ligand field strength of the anions and the order of increasing anion size. No change was observed in the linearity of the Curie–Weiss plots for the perchlorate and acetate. The former anion is too large to serve effectively as a ligand and the latter is so similar in ligand field strength to water that no difference in the magnetic susceptibilities is expected. The bromide did not lose water as rapidly as the corresponding chloride and did not form clearly observed intermediates. This is probably due to the fact that the bromide ion is larger than the chloride and not so strong a ligand. Thus it does not replace ligand water as readily. The large number of intermediate hydrates formed by the nitrate is not easily explained. It may perhaps be due to the fact that the nitrate ion has three equivalent oxygen atoms, any one of which may act as a ligand.

The magnetic data clearly indicated that most of the cobalt(II) ions present in the liquid phase above 50°C were octahedrally coordinated. Previous reflectance spectroscopic evidence, however, indicated that at least some tetrahedrally bonded cobalt(II) species are present in the liquid state for the chloride and bromide[11]. It should be pointed out, however, that the presence of only a small amount of the highly absorbing cobalt(II) species need be present to account for the large change in the reflectance spectra. The liquid phase may be considered as a highly concentrated aqueous solution in which several cobalt(II) species are present in a state of equilibrium. This is supported by the fact that a large increase in the electrical conductivity is also observed. Previous studies have indicated that some tetrahedral species such as $[CoCl_3H_2O]^-$ and $[CoCl_2(H_2O)_2]$ do exist in concentrated cobalt(II) chloride solutions[40,41].

The effects of water vapor on the deaquation reactions studied in this investigation again indicate the importance of the type of furnace atmosphere. The minimum dissociation temperatures of all of the deaquation reactions were increased by the presence of the water vapor; similar effects have previously been noted[42]. Likewise, since the DTA curves in this investigation were obtained with the sample contained in a capillary tube, a self-generated water atmosphere was present during the dissociation reaction. Thus, the minimum deaquation temperatures are higher than those indicated by the TG curves.

Reaction intermediates were more clearly detectable in those curves obtained in the presence of water vapor. This is quite evident in the case of the nitrate. It is possible that the presence of water facilitates the recrystallization of the new hydrate phase in the case of consecutive hydrate dissociations[46]. It is also of interest to note that the presence of water vapor completely changed the nature of the intermediate hydrate for the perchlorate; the 2-hydrate being obtained in an anhydrous atmosphere and the 4-hydrate in a water saturated atmosphere. The water vapor therefore suppresses the evolution of the second two water molecules and perhaps an equilibrium phenomenon is indicated. Both hydrates were observed in an air atmosphere[29].

The effect of the water in the atmosphere *lowered* the reaction temperature of the decomposition of $Co_3(OAc)_5OH$ which is formed during the thermal decomposition of the acetate. In this case the water vapor probably reacted with the basic complex. A similar lowering of the minimum dissociation temperature of a basic compound by water vapor has previously been observed[43].

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