

A comparative study of the thermal dehydration characteristics of $MCl_2 \cdot 2H_2O$ (where $M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}$ and Cu^{2+}) under dynamic condition

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A brief comparative study on the thermal dehydration behavior of the hydrated chlorides of some 3d transition metals (Mn-Cu series) under dynamic or rising temperature condition has been carried out based on the results obtained from the recent investigations on this subject. Several interesting features correlating molecular geometry of the hydrated salts with their thermal stability have been discussed.

Recently, the author has carried out a series of investigation¹ on thermal dehydration and decomposition of hydrated chlorides of some 3d transition metals ($Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$) using the dynamic TG and DTA at different heating rates. This includes not only the study of the mass loss behavior at different steps of dehydration and decomposition, but also the kinetics of these steps with increasing temperature. An attempt has also been made to estimate the heats of dehydration of the dihydrate salts from the area under the corresponding DTA peaks. It is therefore pertinent to compare the results obtained from the above studies with increasing atomic number from Mn to Cu and draw some general conclusions, if any.

Results and discussion

At the outset, let us examine the possible geometry or stereo chemical structures of dihydrate, monohydrate and anhydrous chlorides of all the five metal ions. Though neutral H_2O molecule is a stronger ligand than Cl^- , the actual field strength values as determined by spectroscopic method do not show wide differences^{2,3}. Therefore, H_2O is somewhat intermediate between strong and weak ligand thus providing certain flexibility in the distribution of d electrons in the t_{2g} and e_g orbitals under the octahedral environment. Accordingly, dihydrate chlorides of Mn^{II}, Fe^{II} and Co^{II} form high spin or outer orbital complexes leaving the

Table 1. Geometries of the complex ions corresponding to anhydrous and hydrated chlorides of the transition metal ions of Mn-Cu series and their respective crystal field stabilization energy (cfse) values

Metal ion (d^n)	Dihydrate salt		Monohydrate salt		Anhydrous salt	
	Possible complex ion (geometry)	Type of hybridization (cfse, kJ/mol)	Possible complex ion (geometry)	Type of hybridization (cfse, kJ/mol)	Possible complex ion (geometry)	Type of hybridization (cfse, kJ/mol)
Mn^{2+} (d^5)	$[MnCl_4 \cdot (H_2O)_2]^{2+}$ (Octahedral)	$4s 4p^3 4d^2$ (-)	$[MnCl_5 \cdot H_2O]^{2+}$ (Octahedral)	$4s 4p^3 4d^2$ (-)	$[MnCl_4]^{2+}$ (Tetrahedral)	$4s 4p^3$ (-)
Fe^{2+} (d^6)	$[FeCl_4 \cdot (H_2O)_2]^{2+}$ (Octahedral)	$4s 4p^3 4d^2$ (62.70)	$[FeCl_5 \cdot H_2O]^{2+}$ (Octahedral)	$4s 4p^3 4d^2$ (62.70)	$[FeCl_4]^{2+}$ (Tetrahedral)	$4s 4p^3$ (57.68)
Co^{2+} (d^7)	$[CoCl_4 \cdot (H_2O)_2]^{2+}$ (Octahedral)	$4s 4p^3 4d^2$ (90.71)	$[CoCl_5 \cdot H_2O]^{2+}$ (Octahedral)	$4s 4p^3 4d^2$ (88.62)	$[CoCl_6]^{2+}$ (Octahedral) or (Tetrahedral)	$4s 4p^3 4d^2$ (86.11) $4s 4p^3$
Ni^{2+} (d^8)	$[NiCl_4 \cdot (H_2O)_2]^{2+}$ (Octahedral)	$3d^2 4s 4p^3$ (125.40)	$[NiCl_3 \cdot H_2O]^{2+}$ (Square-planer) or (Tetrahedral)	$3d 4s 4p^2$ (123.73) $4s 4p^3$	$[NiCl_4]^{2+}$ (Tetrahedral)	$4s 4p^3$ (99.48)
Cu^{2+} (d^9)	$[CuCl_4 \cdot (H_2O)_2]^{2+}$ (Distorted octahedral)	$4s 4p^3 4d^2$ (113.70)	-	-	$[CuCl_4]^{2+}$ (Tetrahedral)	$4s 4p^3$ (83.60)

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Note

Table 2. Heats of dehydration and DTA peak temperatures of the different steps of dehydration in air (at 6°C/min) of $MCl_2 \cdot 2H_2O$ where, M represents transition metals of Mn-Cu series

Metal chloride	Loss of 1st mole of H_2O		Loss of 2nd mole of H_2O		Combined loss in single step	
	Heat of dehydration kJ/mol	DTA peak temperature (°C)	Heat of dehydration kJ/mol	DTA peak temperature (°C)	Heat of dehydration kJ/mol	DTA peak temperature (°C)
MnCl ₂	89.8	115.0	81.6	173.0	–	–
FeCl ₂	77.6	121.5	87.0	171.0	–	–
CoCl ₂	25.4	133.0	26.0	175.0	–	–
NiCl ₂	38.0 ^a	–	65.0 ^a	–	53.8	185, 240
	38.1 ^b		75.0 ^b			
CuCl ₂	–	–	–	–	91.5 ^c	107
					128.8	
					106.0 ^c	

^aThe values represent heats of dehydration of the last two moles of water determined during the stepwise dehydration of hexahydrate (Ref. 9) ^bRef. 6 ^cRef. 10

3d level unaffected, but occupying the two e_g orbitals of 4d level to accommodate the two H_2O ligands. Since these orbitals are at higher energy levels, the two H_2O molecules are lost more easily on heating than if they would have occupied 3d orbitals.

On the other hand, it is suggested⁴ that $NiCl_2 \cdot 2H_2O$ form low spin inner orbital octahedral complex similar to that of $CdCl_2 \cdot 2NH_3$ wherein the two NH_3 molecules occupy the two e_g orbitals of 3d orbital by shifting its two electrons to 5s level. Relatively higher charge/radius ratio for Ni^{II} possibly facilitates the bonding of ligands closer to the metal ion and explains higher temperature required for the

two water molecules. However, $CuCl_2 \cdot 2H_2O$ form outer orbital complex with high distortion along the apices of the octahedron. As a result, both the H_2O molecules are lost simultaneously at lower temperature (around 100°C).

Table 1 also gives crystal field stabilization energy (cfse) values for dihydrate, monohydrate and anhydrous salts obtained from the plots of lattice energy against atomic number⁵. Though these values have been obtained independent of their geometries, but are in good agreement, within experimental error, with those calculated from spectroscopic and thermodynamic methods. The structures of the monohydrate salts have been proposed on the basis of

Table 3. Mean activation energy (kJ/mol) values determined by isoconversion method for the dehydration of $MCl_2 \cdot 2H_2O$ (where, M = Mn-Cu series)

Nature of dehydration Step	Mn	Fe ^{II}	Co	Ni	Cu
	Dehydration in static air				
Loss of 1st mole of H_2O	234.4	147.3	90.3	–	–
Loss of 2nd mole of H_2O	121.4	91.2	65.0	–	–
Loss of total H_2O in single step	–	–	–	73.3	71.2
	Dehydration in flowing nitrogen atmosphere				
Loss of 1st mole of H_2O or its fraction	76.1	65.2	125.6	101.3	–
Loss of 2nd mole of H_2O or its fraction	83.7	100.4	101.3	112.2	–
Loss of total H_2O in single step	–	–	–	–	66.5
				76.1 ^a	69.5 ^a

^aRef. 10

nearly similar thermal stability and cfse values of their dihydrate predecessors. Penta coordinated square pyramid or trigonal bipyramid structure has been rejected as these require higher cfse values. In the case of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ square planer geometry appears to be more appropriate as cfse value for tetrahedral configuration is very low (30 kJ/mol) compared to 124 kJ/mol for the former configuration.

For anhydrous chlorides, the concerned metal ions are reported to take, in general, tetrahedral configuration despite higher cfse values. For CoCl_2 both octahedral^{6,7} and tetrahedral⁸ configurations have been suggested because of the small stability difference between geometries.

Table 2 shows the summarized data on DTA peak temperature and the heats of dehydration of the hydrated chlorides of the metal of Mn-Cu series. It can be noted from the table that while the temperature for the loss of first mole of H_2O increases from MnCl_2 to CoCl_2 , the temperature for the loss of second mole of H_2O does not show much variation among the three metal chlorides. For $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ the combined endothermic peaks at 185°C and 240°C are believed to represent the loss of two moles of H_2O suggesting that dehydration of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ takes place at highest temperatures among all the five dihydrate salts. In contrast to $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ the lower temperature required for the dehydration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is due to strong asymmetric distortion of the octahedral complex as stated earlier. Similarly, in the case of anhydrous CuCl_2 the Cl^- at the apex of the tetrahedron has much longer distance than the other three Cl^- . Therefore, unlike other anhydrous salts CuCl_2 shows step-wise dechlorination reaction with increase in temperature¹.

It may be noted from Table 2 that there is no direct relationship between DTA peak temperature and the heat of dehydration which involves not only the heat required to break the coordination bond with metal ion, but also the accompanying structural changes in the process. Relatively higher values of heats of dehydration of MnCl_2 , FeCl_2 and CuCl_2 dihydrates compared to the dihydrates of CoCl_2 and NiCl_2 are due to the fact that the former salts are dehydrated without any preheating, whereas the dihydrates of nickel and cobalt chlorides were prepared by partially dehydrating the normal hexahydrate salts by slow heating in an air oven.

During this process the products undergo necessary structural changes. This is evident from the $\Delta H_{\text{dehd.}}$ values given for the dehydration of the last two moles of H_2O determined from step-wise dehydration of the hexahydrate salts⁹. The combined value of 95 kJ/mol is close to 91.5 kJ/mol obtained by Mohamed and Halawy¹⁰ using the DSC method for the loss of two moles of water in a single step.

Table 3 shows the mean E values obtained by the isoconversion method at different α levels, the range of which is given elsewhere¹. It may be noted that in static air the E values tend to decrease from Mn to Cu, whereas in flowing N_2 atmosphere the E values tend to increase from Mn to Ni with the exception of Cu. The latter values appear to be more appropriate, since in N_2 atmosphere the build-up of H_2O vapour pressure in the vicinity of the sample is prevented. The increasing trend is in tune with the increase in DTA peak temperature and also the difference in cfse value between dihydrate and anhydrous salt which is highest for Ni (*cf.* Table 1). However, Cu^{II} (d^9) behaves differently because of large Jahn-Teller distortion.

References

1. S. B. Kanungo, *J. Indian Chem. Soc.*, 2004, **81**, 664, 750, 842, 921; 2005, **82**, 108.
2. G. Anderegg, "Coordination Chemistry", Vol. 1, ed. A. E. Martell, Van Nostrand Reinhold Corp., New York, 1971.
3. P. George and D. S. Mac Clure, "Progress in Inorganic Chemistry", Vol. 1, ed. F. A. Cotton, Interscience, New York, 1959.
4. N. S. Akhmetov, "General and Inorganic Chemistry", (Engl. Transl.), Mir Publishers, Moscow, 1983, p. 611.
5. S. B. Kanungo, "Proc. 8th Natl Symp on Thermal Analysis", held at Bhubaneswar, December 19-21, 1991, *Indian Thermal Anal Soc.*, Mumbai, pp. 264-269.
6. W. K. Grindstaff and N. Fogel, *J. Chem. Soc. (Dalton)*, 1972, 1476.
7. N. S. Akhmetov, "General and Inorganic Chemistry", (Engl. Transl.), Mir Publishers, Moscow, 1983, p. 597.
8. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley Eastern Ltd., New Delhi, 1990, p. 877.
9. S. B. Kanungo and S. K. Mishra, *Metals, Materials & Processes*, 1997, **9**, 1.
10. M. A. Mohamed and S. A. Halawy, *J. Thermal Anal.*, 1994, **41**, 147.