ELSEVIER

Thermochimica Acta 307 (1997) 143–147

thermochimica
acta

Preparation, characterization and thermal reactivity of *N,N*-dimethylformamide complexes of some transition metal chlorides

V.T. Yılmaz*, Y. Topcu

Ondokuz Mayis University, Chemistry Department, 55139, Kurupelit, Samsun, Turkey

Received 23 May 1997; received in revised form 27 August 1997; accepted 28 August 1997

Abstract

The coordination adducts of $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$ and $CuCl_2$ with DMF were isolated and characterized by elemental analysis, magnetic moments, UV–VIS spectroscopy, IR spectroscopy and thermal analysis techniques. The shift of the CO stretching vibration to low frequency indicated that DMF is bonded through oxygen to the metals. On the basis of spectral and elemental analysis data, the complexes have dimeric and trimeric structures achieved by the chlorine bridges. The complexes do not have melting points and undergo decomposition after dehydration. The decomposition of DMF in the complexes occurs in several stages and the last stages of decomposition always corresponds to decomposition or sublimation of the respective metal chlorides to produce the respective metal. © 1997 Elsevier Science B.V.

Keywords: Dimethylformamide; Metal complexes; UV–VIS–IR spectra; Thermal analysis

1. Introduction

N,N-dimethylformamide (DMF) is the simplest disubstituted amide and is extensively used in laboratory reactions and industrial processes as a solvent [1]. Structural features of DMF have been well established by IR [2,3] and ^1H NMR [3] spectroscopy.

Beside the solvent properties, DMF is also potentially an ambidentate ligand with oxygen and nitrogen as possible donor atoms. The first DMF complex with zinc chloride was reported by Kuhn and McIntyre [4]. The coordination adducts of 2B family such as $Cd_2Cl_4 \cdot 3DMF$ [5] and $Hg_3Cl_6 \cdot 2DMF$ [6] were isolated and characterization and thermochemistry of the DMF adducts, $MX_2 \cdot n$DMF (X=Cl, Br, I; M=Zn, Cd, Hg; n=1,2) were studied [7,8]. Mixed ligand coordination compounds of tin tetrahalides with DMF have also been synthesized [9–14]. However, coordination adducts of DMF with 3*d* transition metals have been less investigated than those of the other metals. Only the $Mn(DMF)_6(ClO_4)_3$ [15] and $Ni(DMF)_6(ClO_4)_2$ [16] complexes appeared in the literature. In this work, new coordination adducts of some first transition metal chlorides with DMF were synthesized and their spectral and thermal analysis were studied.

2. Experimental

2.1. Preparation of complexes

Metal chlorides and DMF were obtained commercially (Merck) and DMF was distilled before use.

The coordination adducts were prepared by dissolving 1 mmol of anhydrous metal chlorides in excess

---

*Corresponding author. Fax: 00 90 362 4576081.

PII S0040-6031(97)00322-5

amount of DMF. The solutions were stirred for 2 h and allowed for crystallization. The excess DMF was removed in vacuo. The crystals were then washed with ethanol and kept in a desiccator.

2.2. Instrumentation

UV–VIS spectra were obtained with a UNICAM UV2 spectrometer in aqueous solutions. IR spectra were recorded with a MATTSON 1000 FTIR spectrometer using KBr pellets. Magnetic susceptibilities at ambient temperatures were measured using a SHERWOOD SCIENTIFIC MXI model Gouy magnetic balance.

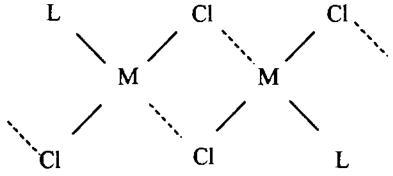
C, H, and N elemental analyses were carried out at the Marmara Research Center (Gebze). The chlorine contents were determined by the conventional Mohr's method [17].

A Rigaku TG8110 thermal analyser was used to record the simultaneous TG, DTG, and DTA curves. The experiments were performed in static nitrogen atmosphere in the range 20–1000°C. The heating rate was 10 K min^{-1} and the sample sizes ranged in mass from 5 to 10 mg. Highly sintered α-Al_2O_3 was used as the reference material.

3. Results and discussion

3.1. Synthesis and magnetic susceptibilities

The analytical data for the complexes are given in Table 1. The data are in agreement with the formulae proposed. However, the experimental chlorine contents of the Fe(III) and Co(II) complexes are somewhat different from the calculated values. This is due to the interference of these metal ions during the determination [17]. All the complexes are very sensitive to moisture and soluble in water. The study of the DMF adducts of the zinc group metal halides indicated that these coordination adducts exist as dimeric structures with a halogen bridging the metals [8]. On the basis of this information, it is suggested that the complexes isolated have dimeric trans symmetric and trimeric structures as illustrated below.



The magnetic moment values are given in Table 1. These values suggest that the complexes are of the high-spin type with tetrahedral coordination. The Fe(III) complex is also of the high-spin type, but has the octahedral coordination.

3.2. Spectral analysis

The results of electronic spectra are given in Table 2. All the complexes comprise a broad composite band in the UV region. The band exhibits mainly three maxima due to intraligand transitions of DMF. The Mn(II) and Fe(III) have d^5 electronic arrangement and do not give any peak in the visible region. Co(II), Ni(II) and Cu(II) exhibit characteristic *d–d* bands. The *d–d* transitions are characteristic of the relevant geo-

Table 1
Analytical and magnetic data for the complexes of DMF

Complex	M.W. in g mol^{-1}	Colour	%C [a]	%H [a]	%N [a]	%Cl [a]	μ_{eff} in BM
$Mn_2Cl_4 \cdot 2DMF \cdot H_2O$	415.88	Pale pink	17.21	3.60	6.05	35.34	4.57
$C_6H_{16}N_2O_3Cl_4Mn_2$			(17.31)	(3.84)	(6.73)	(34.09)	
$Fe_2Cl_6 \cdot 3DMF \cdot 2H_2O$	579.60	Pale yellow	18.70	3.73	6.93	38.23	5.28
$C_9H_{25}N_3O_5Cl_6Fe_2$			(18.63)	(4.31)	(7.24)	(36.69)	
$Co_2Cl_4 \cdot 2DMF \cdot 2H_2O$	441.86	Blue	15.17	3.98	5.53	38.16	3.83
$C_6H_{16}N_2O_4Cl_4Co_2$			(16.29)	(4.07)	(6.34)	(32.09)	
$Ni_2Cl_4 \cdot 2DMF \cdot 5H_2O$	495.38	Yellow	15.58	4.62	5.51	28.26	2.69
$C_6H_{24}N_2O_7Cl_4Ni_2$			(14.53)	(4.85)	(5.65)	(28.62)	
$Cu_3Cl_6 \cdot 2DMF$	549.60	Light brown	13.32	2.56	4.80	37.60	1.55
$C_6H_{14}N_2O_2Cl_6Cu_3$			(13.10)	(2.55)	(5.09)	(38.71)	

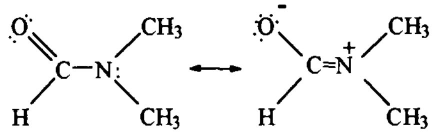
[a] Calculated values are given in paranthesis.

Table 2
UV/VIS and IR spectral data for the complexes of DMF

Compound	λ_{max} in nm					ν in cm^{-1}		
	Ligand			d–d	Assignment	$\nu_{(C=O)}$	$\nu_{(N-C=O)}$	$\nu_{(M-O)}$
DMF	207	232	270	—	—	1677	634	—
$Mn_2Cl_4{\cdot}2DMF{\cdot}H_2O$	212	235	275	—	—	1650	685	562
$Fe_2Cl_6{\cdot}3DMF{\cdot}2H_2O$	213	239	291	—	—	1647	694	396
$Co_2Cl_4{\cdot}2DMF{\cdot}2H_2O$	208	230	281	510	$^4A_2 \rightarrow {}^4T_{1(p)}$	1653	692	574
$Ni_2Cl_4{\cdot}2DMF{\cdot}5H_2O$	217	238	282	706	$^3T_1 \rightarrow {}^3T_{1(p)}$	1657	709	596
$Cu_3Cl_6{\cdot}2DMF$	209	232	—	814	$^2T_2 \rightarrow {}^2E_2$	1656	710	634

metry around the metal ions and were assigned as given in Table 2 [18].

The important IR data of the complexes are listed in Table 2. The C–O stretching peak of DMF at 1677 cm^{-1} has been of great importance in the study of the bonding and complexing of DMF by other chemical species. The C–O bond has been frequently regarded as having considerable double bond character as being a resonance hybrid of the following structures.



I II

Bonding of a metal ion to the O atom of coordinated DMF stabilizes electronic structure I, lowers the bond order of the C–O bond and decreases the frequency of the C–O vibration, while bonding of a metal ion to the N atom stabilizes the structure II, increases the C–N bond order [2,3,19].

The vibrational spectra of the metal complexes showed that the C–O stretching peak of DMF at 1677 cm^{-1} significantly shifted to low frequency upon complexation (Table 2). However, an opposite shift was observed for the C–N frequency at 634 cm^{-1}. These results clearly indicate that the metal ions are coordinated by the oxygen atom of DMF. The low intensity bands in the region 400–650 cm^{-1} were attributed to the M–O vibrations [20].

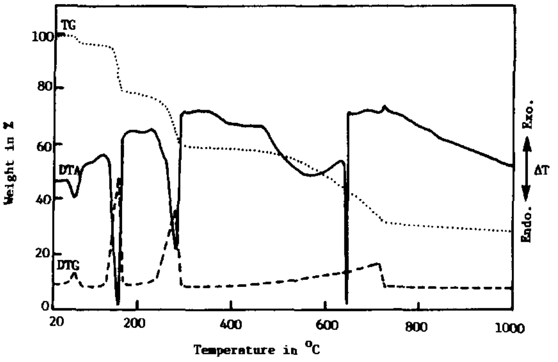


Fig. 1. Thermal analysis curves of $Mn_2Cl_4{\cdot}2DMF{\cdot}H_2O$.

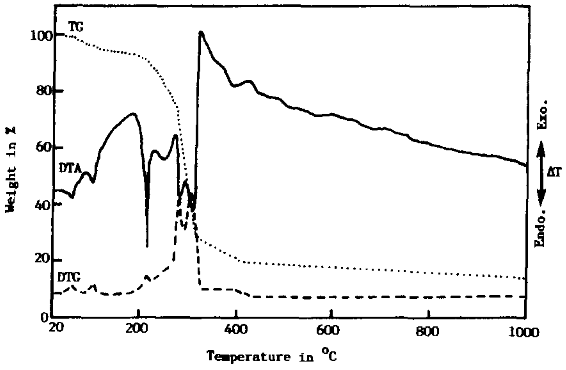


Fig. 2. Thermal analysis curves of $Fe_2Cl_6{\cdot}3DMF{\cdot}2H_2O$.

3.3. Thermal analysis

The simultaneous TG–DTA data of the complexes are summarized in Table 3 and the thermal analysis curves are illustrated in Figs. 1–5. In general, all the complexes do not have a melting point and decompose after dehydration. The stoichiometries of the coordination adducts established by elemental analysis are confirmed by the total weight loss determinations. After dehydration of the complexes, the desolvation of DMF occurs in several steps and the last stage always corresponds to the decomposition or sublima-

Table 3
Thermoanalytical data for the complexes of DMF

Complex	Stage	Temperature range in°C	DTG max in°C	Weight loss in %		Decomposition product
				Found	Calcd.	
$Mn_2Cl_4{\cdot}2DMF{\cdot}H_2O$	1	20–110	68	4.66	4.33	$Mn_2Cl_4{\cdot}2DMF$
	2	123–203	158	17.53	17.57	$Mn_2Cl_4{\cdot}DMF$
	3	226–300	281	17.94	17.57	Mn_2Cl_4
	4	455–700	650	26.59	—	Mainly Mn
$Fe_2Cl_6{\cdot}3DMF{\cdot}2H_2O$	1	20–76	65	3.05	3.10	$Fe_2Cl_6{\cdot}3DMF{\cdot}H_2O$
	2	76–147	107	3.14	3.10	$Fe_2Cl_6{\cdot}3DMF$
	3	172–471	215, 285, 295	74.00	74.51	Fe
$Co_2Cl_4{\cdot}2DMF{\cdot}H_2O$	1	60–136	110	8.95	8.15	$Co_2Cl_4{\cdot}2DMF$
	2	199–319	232, 258, 312	34.84	33.09	Co_2Cl_4
	3	329–941	700, 822	29.95	32.09	Co
$Ni_2Cl_4{\cdot}2DMF{\cdot}5H_2O$	1	67–102	94	19.54	18.19	$Ni_2Cl_4{\cdot}2DMF$
	2	102–269	132, 235	28.04	29.51	Ni_2Cl_4
	3	474–790	734	26.43	28.62	Ni
$Cu_3Cl_6{\cdot}2DMF$	1	154–256	108, 232	26.93	26.60	Cu_3Cl_6
	2	256–655	188, 229, 427, 635	73.07	73.40	—

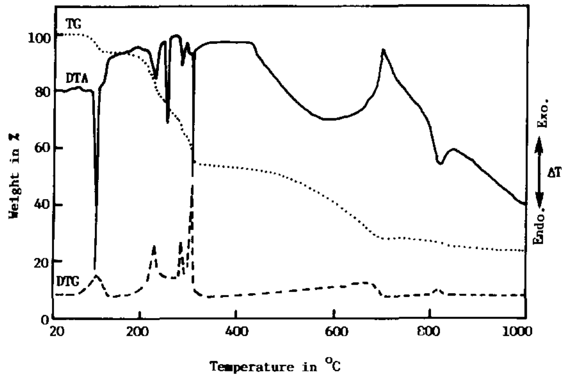


Fig. 3. Thermal analysis curves of $Co_2Cl_4{\cdot}2DMF{\cdot}2H_2O$.

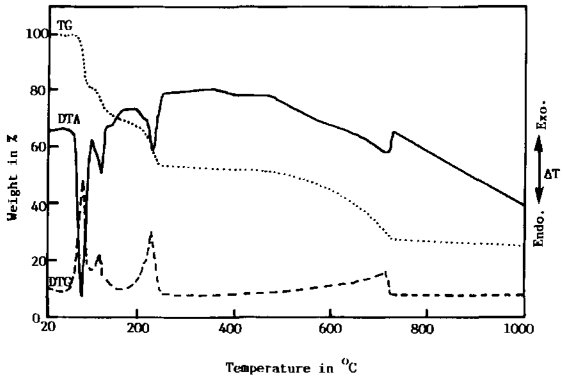


Fig. 4. Thermal analysis curves of $Ni_2Cl_4{\cdot}2DMF{\cdot}5H_2O$.

tion of the respective metal halide at higher temperatures. The experimental weight loss values are in good agreement with the calculated values. The final decomposition products were identified by the conventional chemical analysis methods.

3.3.1. $Mn_2Cl_4{\cdot}2DMF{\cdot}H_2O$

The complex shows four steps of decomposition in TG and four peaks in DTA (Fig. 1). The first endothermic peak at 68°C in the temperature range 20–110°C corresponds to loss of the crystallization water. The DMF molecules were released in two endothermic stages with maxima at 158 and 281°C in the range 120–300°C. The last stage corresponds to both melting and decomposition of $MnCl_2$ to produce a compound or a mixture mainly composed of Mn. The end product could not be characterized.

3.3.2. $Fe_2Cl_6{\cdot}3DMF{\cdot}2H_2O$

The thermal analysis curves of the complex are shown in Fig. 2. The loss of the water molecules takes place in two endothermic decomposition steps in the

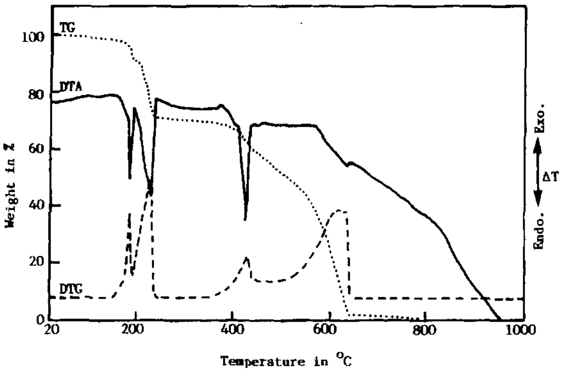


Fig. 5. Thermal analysis curves of $Cu_3Cl_6 \cdot 2DMF$.

range 20–150°C. The decomposition of the anhydrous complex starts at 170°C with melting and ends at 470°C. This stage consists of indistinguishable steps and involves decomposition of both DMF and $FeCl_3$ to give Fe.

3.3.3. $Co_2Cl_4 \cdot 2DMF \cdot 2H_2O$

The first step in the decomposition of the complex involves endothermic dehydration at 110°C. The anhydrous complex undergoes complete decomposition in three steps between 200 and 320°C to produce $CoCl_2$. The TG curve of this complex shows three consecutive steps of decomposition of DMF, although the DTA curve includes four peaks for this stage (Fig. 3). The peak at 258°C without any weight loss is probably due to melting of the intermediate formed. The last stage corresponds to the decomposition of $CoCl_2$ to give Co.

3.3.4. $Ni_2Cl_4 \cdot 2DMF \cdot 5H_2O$

The first step in the decomposition sequence corresponds to the dehydration of the complex. The evolution of DMF present in the complex occurs in the range 102–270°C with two maxima at 132 and 235°C to give $NiCl_2$. The final step corresponds to the decomposition of $NiCl_2$ to produce Ni.

3.3.5. $Cu_3Cl_6 \cdot 2DMF$

The complex exhibits four distinct steps in decomposition as shown in Fig. 5. The removal of DMF present in the complex takes place in the first and second stage in the range 154–256°C to give $CuCl_2$. The respective chloride begins to decompose with melting at higher temperatures and the last two stages in decomposition correspond to both melting and sublimation of $CuCl_2$.

Acknowledgements

The authors wish to thank Ondokuz Mayis University for the financial support given to the project.

References

[1] J.J. Lagowski, The Chemistry of Non-Aqueous Solvents, Vol. 2, Academic Press, London, 1967.
[2] G. Durgaprasad, D.N. Sathyanaroyana, C.C. Patel, Bull. Chem. Soc. Jpn. 44 (1971) 316.
[3] G. Kaufman, M. Leroy, Bull. Soc. Chim. Fr. 1 (1967) 402.
[4] S.J. Kuhn, J.S. McIntyre, Can. J. Chem. 43 (1965) 375.
[5] R.C. Paul, B.R. Sreenathan, Indian J. Chem. 4 (1966) 348.
[6] I. Baxter, G.A. Swan, J. Chem. Soc. 2 (1965) 3011.
[7] R.C. Paul, B.R. Sreenathan, Indian J. Chem. 4 (1966) 382.
[8] O.A. DeOliveira, A.P. Chagas, C. Airoldi, Inorg. Chem. 22 (1983) 136.
[9] R.C. Paul, B.R. Sreenathan, S.L. Chadha, J. Inorg. Nucl. Chem. 28 (1966) 1225.
[10] M.F. Farona, J.G. Graselli, Inorg. Chem. 6 (1967) 1675.
[11] T.N. Srivastava, S.K. Tandon, N. Bhakru, J. Inorg. Nucl. Chem. 38 (1976) 2311.
[12] D. Tudela, V. Fernandez, Z. Anorg. Allg. Chem. 512 (1986) 215.
[13] J.D. Tornero, V. Fernandez, D. Tudela, J. Mol. Struct. 143 (1986) 171.
[14] D. Tudela, F. Rey, Z. Anorg. Allg. Chem. 575 (1989) 202.
[15] J.P. Prabhakaran, C.C. Patel, J. Inorg. Nucl. Chem. 30 (1968) 867.
[16] V. McKee, T. Metcalfe, J. Wikaira, Acta Cryst. C52 (1996) 1139.
[17] N.H. Furman, Standard Methods of Chemical Analysis, Vol. 1, 6th ed., Van Nostrand Company, Canada, 1968.
[18] A.B. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.
[19] E.W. Randall, C.M.S. Yoder, J.J. Zuckerman, Inorg. Chem. 5 (1966) 1966.
[20] K. Nakamato, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.