

Available online at www.sciencedirect.com

s



Journal of Molecular Structure 657 (2003) 385-393

www.elsevier.com/locate/molstruc

# Spectroscopic and thermal studies of Mn(II), Co(II) and Ni(II) bromide *m*-methylaniline complexes

K. Golcuk\*, A. Altun, M. Kumru

Department of Physics, Fatih University, B.CEKMECE, Istanbul 34900, Turkey

Received 20 May 2003; revised 2 July 2003; accepted 3 July 2003

# Abstract

The complexes of the MBr<sub>2</sub>L<sub>2</sub> [M: Mn(II), Co(II) and Ni(II); L: *m*-methylaniline (mMA)] form have been prepared and characterized by their elemental analyses, thermogravimetric analyses, magnetic moment measurements, UV-vis, IR and Raman spectral studies. Elemental analysis suggests the stoichiometry to be 1:2 (metal:ligand). Thermal decomposition studies, using thermogravimetry show that the intermediate metal complexes are formed for complexes during their decomposition processes, the metal oxide being finally produced in each case. IR and Raman bands of the complexes have been assigned as compared with the free ligand. Coordination effects on the internal modes of mMA have been discussed. A polymeric octahedral geometry around metal ion with bridging bromides has been proposed for the Mn(II) and Ni(II) complexes, while tetrahedral geometry around Co(II) ion with  $C_{2\nu}$  symmetry is suggested for the Co(II) complex. © 2003 Elsevier B.V. All rights reserved.

Keywords: MnBr2, CoBr2 and NiBr2 complexes; m-methylaniline; Spectroscopy; Thermal analysis; Structure

## 1. Introduction

Aniline and its derivatives are of great industrial importance. These compounds are widely used for producing polyurethanes, rubbers, pesticides and dyes and also found in the environment [1]. Recently, their toxicity effects to *Daphnia magna* were also studied [2]. Hence, understanding of their molecular properties and the reactions they experience is very important. Besides, their metal(II)halide complexes have been interested for decades [3-12]. As a continuation of previous works [10-12], we report

thermogravimetric (TG) behaviors, magnetic moments, electronic spectra and vibrational spectra of the metal(II) [Mn(II), Co(II) or Ni(II)] bromide with *m*-methylaniline complexes in the present study. A detailed vibrational bands analysis of each metal complex is also given. The spectroscopic investigations are used to obtain further information about the local structure around the metal ions.

## 2. Experimental

All the chemicals used were reagent grade (Fluka– Aldrich). The polycrystalline complexes were prepared using the method given in Refs. [10,11].

<sup>\*</sup> Corresponding author. Tel.: +90-212-8890810; fax: +90-212-8891142.

E-mail address: kgolcuk@fatih.edu.tr (K. Golcuk).

Composition and purity (C, H, N, and M) were determined by microanalysis (see Table 1).

Electronic spectra in EtOH were recorded on a Perkin Elmer Lambda 9 UV–VIS–NIR spectrometer in the range 190–1100 nm.

Measurements of magnetic moments at room temperature were made using the Evans method with a Sherwood Sci. magnetic balance. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.

Thermal analyses were made on a Mettler Toledo TG50 thermobalance under a  $N_2$  flow (flow rate,  $30 \text{ cm}^3 \text{ min}^{-1}$ ). The samples were heated in an  $Al_2O_3$  crucible at rate of 10 °C min<sup>-1</sup>.

The FT-IR spectra were recorded using KBr discs over range 4000-400 cm<sup>-1</sup> on a Perkin Elmer Paragon 1000 FT-IR. The 500-200 cm<sup>-1</sup> region spectra were recorded using polyethylene discs over the range 500-200 cm<sup>-1</sup> on a Mattson 2030 Galaxy FT-IR spectrometer.

Raman spectra were recorded on a Bruker RFS 100/S FT-Raman Spectrometer in the range  $3600-70 \text{ cm}^{-1}$ . A 1.5 W Nd–YaG air-cooled laser delivering excitation wavelength of 1064 nm was used.

## 3. Results and discussion

Elemental analysis data, listed in Table 1, suggest that the complexes have 1:2 (M:L) stoichiometry. Based on the elementary chemical analysis has been suggested, for all the compounds,  $[MBr_2(mMA)_2]$  form.

#### 3.1. Vibrational spectroscopy

Analyses (%) of the metal complexes

Table 1

In order to get data conceiving the ligand way of coordination to the metal ions, the vibrational spectra of the complexes have been considered. The only coordination site for the ligand *m*-methylaniline (mMA) is the nitrogen atom of the amine group. Hence, we pay attention to  $-NH_2$  group vibrations upon complexation. The FT-IR spectra of mMA and its complexes are shown together in Fig. 1. The Raman spectrum of cobalt complex exhibits very strong florescence, covering all the vibrational bands. Hence, we could not obtain a clear Raman spectrum of Co(II) complex for several attempts. We only give FT-Raman spectra of the Mn(II) and Ni(II) complexes and free ligand in Fig. 2.

All observed vibrational bands and their assignments are given in Table 2. Vibrational mode assignments of the free mMA are based on ab initio and DFT calculations and fully reported in Ref. [13]. A band for band correspondence is also considered for the spectra of the compounds.

The  $\nu$  NH asymmetric and symmetric stretching bands are shifted towards lower wavenumbers on the formation of the complexes. This would suggest that the N atom of the amine group coordinates to metal ion [3–12]. The shifting to the lower frequencies can be explained as a weakening of the N–H bonds resulting from the electron drainage from the nitrogen atom due to its coordination to the metal atom [10–12].

The NH<sub>2</sub> scissoring frequency at  $1622 \text{ cm}^{-1}$  in the mMA spectrum is lowered  $50 \text{ cm}^{-1}$  by coordination. The change in hybridization of nitrogen orbitals and therefore the alteration of HNH angle decreases NH<sub>2</sub> scissoring force constant and causes the shifts upon the complexations. We have assigned the band observed at  $1293 \text{ cm}^{-1}$  to the  $\nu$  CN stretching for free mMA. Vibrations of this mode occur at lower frequencies in the complexes, in line with the decrease in the C=N double bond character [11].

Compound	Colour	Found (Calc.)%					
		M	С	Ν	Н		
$[MnBr_2(mMA)_2]_n$	Pale pink	12.88(12.80)	38.90(39.19)	6.49(6.53)	4.18(4.23)		
[CoBr <sub>2</sub> (mMA) <sub>2</sub> ]	Blue	13.49(13.61)	38.69(38.83)	6.45(6.47)	4.26(4.19)		
$[NiBr_2(mMA)_2]_n$	Light yellow	13.23(13.56)	39.29(38.85)	6.89(6.47)	4.15(4.19)		





Fig. 1. FT-IR spectra of (a) mMA, (b)  $[MnBr_2(mMA)_2]_n$ , (c)  $[CoBr_2(mMA)_2]$  and (d)  $[NiBr_2(mMA)_2]_n$ .

The metal-sensitivity of the  $\nu$  NH and  $\nu$  CN bands is in the sequence Co < Ni < Mn which is the inverse order of the masses of the metal atoms.

Jungbauer and Curran [14] reported a study of some deuterated aniline metal halide complexes

and suggested that the  $NH_2$  wagging vibration was observed as a very strong and coordination sensitive band in the region  $1185-1000 \text{ cm}^{-1}$ , while it appeared at  $670 \text{ cm}^{-1}$  in the IR spectrum of aniline. The similar shifts were also observed in



Fig. 2. FT-Raman spectra of (a) mMA, (b)  $[MnBr_2(mMA)_2]_n$  and (c)  $[NiBr_2(mMA)_2]_n$ .

387

388

Table 2

Infrared and Raman	frequencies	of mMA	and	metal	complexes
--------------------	-------------	--------	-----	-------	-----------

mMA		$[MnBr_2(mMA)_2]_n$		[CoBr <sub>2</sub> (mMA) <sub>2</sub> ]	$[NiBr_2(mMA)_2]_n$		Assignment
IR	Ra	IR	Ra	IR	IR	Ra	
3435 s		3328 m	3330 w	3264 s	3317 s	3316 w	$\nu$ NH (asym.)
3354 s	3353 m,br	3296 m	3297 w	3215 s	3236 s	3235 s	$\nu$ NH (sym.)
3218 m	3212 m,br	3124 w,br		3116 m	3121 m	3122 w	$2 \times 1620$ over
3034 m	3046 s	3028 w,sh	3046 s		3034 w	3053 s	$\nu$ CH ring
3015 m,sh	3012 s	3012 w.sh	3014 m,sh	3033 m			$\nu$ CH ring
2975 m.sh	2974 m		2976 w		2966 vw	2977 w	$\nu$ CH ring
2946 m,sh			2951 w,sh			2947 w	$\nu$ CH ring
2919 m	2919 s	2914 w	2917 s	2918 m	2919 w	2917 s	$\nu$ CH <sub>3</sub> (asym.)
2857 w	2857 m,sh	2858 w	2860 w	2855 vw	2855 vw	2852 w.sh	$\nu$ CH <sub>3</sub> (sym.)
1622 vs	1620 s	1572 s		1572 vs	1573 s		NH <sub>2</sub> (sciss.)
		1616 s	1614 s	1615 s	1617 s	1614 m,sh	$\nu  CC  ring$
1591 vs	1590 m	1598 s	1598 s	1596 s	1594 m,sh	1597 s	$\nu$ CC ring
1513 m.sh	1514 vw	1516 vw.sh		1517 vw	1516 vw		$\nu$ CC ring
1493 vs	1493 vw	1494 vs	1494 w	1492 vs	1496 vs		$\nu$ CC ring
1469 s		1466 s	1463 vw	1470 s	1467 s	1472 m	$\beta$ CH <sub>3</sub> (asym.)
1443 m.sh	1447 w.br		1440 w.br	1436 m.sh	1437 m.sh	1440 w.br	$\beta$ CH <sub>3</sub> (asym.)
1381 w	1378 m	1374 w	1378 s	1374 w	1374 w	1382 m	$\beta$ CH <sub>3</sub> (svm.)
1314 m	1313 m.sh	1313 vw	1312 w		1309 vw	1313 vw	βCH
1293 s	1293 s	1264 m	1278 m.sh.	1277 w	1282 vw	1284 w.sh	$\nu CN$
			1268 s	1257 s	1262 m	1261 s	$\nu CN$
1170 s	1166 m	1170 m	1170 m	1167 w	1170 m	1168 m	$\beta$ CH ring
			1146 vw	1144 w	1143 w	1139 vw	$\nu$ CCH <sub>2</sub>
1077 w	1075 w	1086 m	1085 vw	1094 vs	1087 m	1087 m	$\beta$ NH <sub>2</sub> (rock.)
996 m	996 m	990 vs	1000 vs	996 m sh	999 m	1000 vs	$\beta CCC ring$
926 w	928 w	918 vs	919 w	916 m	919 m	920 m	$\beta$ CCC ring
870 m	20 H	882 s	886 w	889 m	886 w	899 w	$\gamma$ CH ring: $\gamma$ CCC
855 m		854 m	866 w	867 m	862 w		$\gamma$ CH ring: $\gamma$ CCC
775 vs	784 w	776 vs	778 w	780 vs	773 vs		$\gamma$ CH ring: $\gamma$ CCC
726 m sh	738 s	730 m	728 s	729 m	733 m	733 s	Breathing
691 vs	1000	690 vs	120 0	688 vs	690 s	690 m	$\gamma$ CCC ring
655 <sup>a</sup>		1022 vs	1025 m	1035 w	1043 vs	1058 s	$\gamma \text{ NH}_2$ (wagg.)
557 m		557 s		568 m	575 w	575 vw	$\gamma CCC ring$
538 m	543 m	543 m	545 s	546 w	549 w	549 m	$\beta$ CCC ring
000 111	518 m	518 vw.sh	520 s	518 vw	0.0	518 s	$\beta$ CCC ring
	431 w	441 s	441 vw	445 m	445 m	450 w	$\gamma$ CCC ring
		412 s	419 w	420 m	415 s	417 vw	$\nu$ (M–N)
		329 m	331 m	399 m	372 m. br		$\nu$ (M-N)
		0 <u>_</u> ) III	001 m	577 m	354  m br	357 m.br	
	294 m	296 m	293 m	292.8	297 s	297 m	B CNH <sub>2</sub> : B CH <sub>2</sub>
	27111	285 m	293 m 284 m	292 8	277 8	2)7 m	$p$ er ( $n_2$ , $p$ er $n_3$
	234 m	570 s	574 m	652 m	618 s	608 m	$\gamma$ NH <sub>2</sub> (twist)
	20111	0100	<i>c</i> , , , , , ,	635 m	010 5	000 111	<i>f</i> 1 (11 <sub>2</sub> (01150))
		257 m		246 s	253 w		NMN deformation
		240 m		210 5	235  w sh		i deformation
	218 m	221 m	221 s	219 m	215 \$	220 s	γ CNH <sub>2</sub> γ CCC ring
	210 m	221 111	221 3	234 s	210 0	220 3	$\nu$ (M-Br).
				210 \$			$\nu$ (M-Br).
			192 m	210 5		194 s	$\nu (M-Br)_{L}$
			167 m			152 m	$\nu (M-Br)_{b}$
			107 111			10 <b>2</b> m	

Key:  $\nu$ , stretching;  $\beta$ , in plane deformation;  $\gamma$ , out-of-plane deformation s, strong; vs, very strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

<sup>a</sup> Mode has not been observed, but has been found based on ab initio and DFT calculations [13].

our previous works for some metal bromide and iodide mMA complexes [10–12]. We therefore assign the IR bands at 1022, 1035 and 1043 cm<sup>-1</sup> to the NH<sub>2</sub> wagging mode for the Mn(II), Co(II) and Ni(II) complexes, respectively. The explicit metal-sensitivity can be explained directly by mechanical coupling of this mode with M-N vibrations [15].

The weak band at  $1077 \text{ cm}^{-1}$  is attributed to NH<sub>2</sub> rocking mode of free mMA, while it is shifted towards the upper frequencies by complex formation. A study of normal coordinate analysis on aniline revealed that

the band at 216 cm<sup>-1</sup> (NH<sub>2</sub> twisting mode) was found at 605 cm<sup>-1</sup> in aniline–Cd complex [9]. Hence, we have assigned the 652–570 cm<sup>-1</sup> region bands of the complexes to the NH<sub>2</sub> twisting vibrations.

A very intense band is found near  $1000 \text{ cm}^{-1}$  in both Raman spectra of mMA and its complexes, indicating the meta-disubstituted ring. This band is due to a symmetrical in plane ring deformation [13].

The upward shifts of the  $NH_2$  rocking and wagging vibrations follow the sequence Ni > Mn. This order obeys the Irving–Williams stability sequence and can be correlated with the increase in the second ionization potential of the metals.

The metal-ligand bands are helpful for determining the local structure around metal ions. It is considered that the metal-ligand vibrations occur below 500 cm<sup>-1</sup> [3–12]. Assignments of the  $\nu$  (M– N) and  $\nu$  (M–Br) vibrations, listed in Table 2, have been given carefully by considering the internal modes of mMA and comparing with literature reports [3–16]. The 500–200 cm<sup>-1</sup> region spectra of the complexes are shown in Fig. 3.

For the Co (II) complex, the medium IR bands at 420 and 399 cm<sup>-1</sup> have been ascribed as  $\nu$  (Co–N) stretching vibrations. The terminal Co–Br bond stretching, i.e.  $\nu$  (Co–Br)<sub>t</sub> bands occur at 230 and

210 cm<sup>-1</sup> [4–6]. In [CoBr<sub>2</sub>(mMA)<sub>2</sub>], the metal ion is involved in a tetrahedral N<sub>2</sub>CoBr<sub>2</sub> skeleton. Assuming  $C_{2\nu}$  symmetry for this complex, both the antisymmetric and symmetric CoBr<sub>2</sub> and CoN<sub>2</sub> stretching vibrations are IR active [16]. The  $\nu$  (Co–Br)<sub>t</sub> and  $\nu$ (Co–N) stretching vibrations can be described with A<sub>1</sub> + B<sub>1</sub> and A<sub>1</sub> + B<sub>2</sub> representations, respectively. Thus, the low frequency spectrum is consistent with previously reported tetrahedral Co(II) complexes [3–6,14,16].

The stretching vibrations of the bridging M-Br-M bonds, i.e.  $\nu$  (M–Br)<sub>b</sub>, should appear below 200 cm<sup>-1</sup> [17]. In Raman spectrum of Mn(II) complex (see Fig. 2(b)), the 192 and 167 cm<sup>-1</sup> bands are assigned to  $\nu$  $(Mn-Br)_b$ . Similarly, the 194 and 152 cm<sup>-1</sup> bands in Raman spectrum of Ni(II) complex (see Fig. 3(c)) are due to the stretching bands of bridging Ni-Br-Ni bonds, i.e.  $\nu$  (Ni-Br)<sub>b</sub>. Hence, the appearance of the  $\nu$ (M-Br)<sub>b</sub> vibrations indicates a polymeric octahedral structure around metal ions with exclusively bridging bromides for  $[MnBr_2(mMA)_2]_n$  and  $[NiBr_2(mMA)_2]_n$ complexes, where *n* shows the polymeric character of the complexes. As a result, the local environments for both Mn and Ni ions consist of polymeric chains in which each metal atom is surrounded by four bromine atoms and two nitrogen atoms of the ligands, as also



Fig. 3. The  $500-200 \text{ cm}^{-1}$  region spectra of (a) [NiBr<sub>2</sub>(mMA)<sub>2</sub>]<sub>n</sub>, (b) [MnBr<sub>2</sub>(mMA)<sub>2</sub>]<sub>n</sub> and (c) [CoBr<sub>2</sub>(mMA)<sub>2</sub>].



Fig. 4. The proposed molecular structure of (a)  $[CoBr_2(mMA)_2]$  and (b)  $[MnBr_2(mMA)_2]_n$  and  $[NiBr_2(mMA)_2]_n$  complexes (M: Mn, Ni; N: nitrogen atom of the mMA).

reported in aniline complexes [3,5,8,16]. The proposed molecular structures of the complexes are shown in Fig. 4.

The coordination number effect on metal-ligand vibration frequencies is known to be a substantial one [4]. The decreased coordination number which accompanies substitution of Co(II) by Mn(II) is expected to lead to a increase in  $\nu$  (M–N) as is observed. Substitution of Ni(II) by Co(II) is expected to cause an decrease in  $\nu$  (M–N). This result arises from the bonding capacity of the metal ion being distributed over more bands with consequently lower metal-ligand force constants [4]. If the coordination number remains unchanged,  $\nu$  (M–N) bands follow the sequence Mn < Ni. The difference between the frequencies of corresponding  $\nu$  (M–N) bands in each Mn-Ni pair might be attributed to the fact that the Ni(II) complex is stabilized by crystal field splitting whereas the Mn(II) complex is not.

The very strong Raman bands below  $100 \text{ cm}^{-1}$  are ascribed as the lattice mode of the solid complexes [18] and couple with torsional mode of CH<sub>3</sub>.

#### 3.2. UV-vis spectroscopy and magnetochemistry

The electronic spectral data and magnetic moment values of the complexes are given in Table 3. The UV-vis spectrum of Mn(II) complex shows bands around 18315 and 24271 cm<sup>-1</sup>. Both of the d-d transitions are spin forbidden and therefore of low intensity. The complex is pale pink in color. The bands at 24271 and 18315 cm<sup>-1</sup> correspond to  ${}^{6}A_{1g}(S) \rightarrow {}^{4}A_{1g}(G)$ ,  ${}^{4}E_{g}(G)$  and  ${}^{6}A_{1g}(S) \rightarrow {}^{4}T_{1g}(G)$ transitions, respectively. The spectrum bands are consistent with those predicted six coordinated polymeric octahedral Mn complexes [5]. This geometry is confirmed by the value of magnetic moment  $(\mu_{\rm eff} = 5.80 \text{ BM})$  as well, which is a characteristic of high spin octahedral Mn(II) complex [19]. The magnetic moment value of the complex is slightly lower than spin-only value of a Mn(II) ion, showing Mn–Mn interaction.

In the UV–vis spectrum of Ni(II) complex, two bands have been observed at 12820 and 23809 cm<sup>-1</sup>. The spin allowed electronic transitions

K. Golcuk et al. / Journal of Molecular Structure 657 (2003) 385-393

Table 3 UV-vis spectral data, colors and magnetic moments of the metal complexes

Compound	Color	Band position (cm <sup>-1</sup> )	Transition	$\mu_{\mathrm{eff}}$ (BM
$[MnBr_2(mMA)_2]_n$	Pale pink	18315 24271 14925	${}^{6}A1_{g}(S) \rightarrow {}^{4}T_{1g}(G)$ ${}^{6}A_{1g}(S) \rightarrow {}^{4}A_{1g}(G), {}^{4}E_{g}(G)$ ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$	5.80 4.73
[CoBr <sub>2</sub> (mMA) <sub>2</sub> ]	Blue	15625 16077 16649	${}^{4}A_{2}(F) \rightarrow {}^{2}E(G)$ ${}^{4}A_{2}(F) \rightarrow {}^{2}T_{1}(G)$ ${}^{4}A_{2}(F) \rightarrow {}^{2}T_{2}(G)$	
$[NiBr_2(mMA)_2]_n$	Light yellow	12820 23809	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$	3.20

for d<sup>8</sup> octahedral Ni(II) ion are expected from  ${}^{3}A_{2}(F)$  ground state to  ${}^{3}T_{2g}(F)$ ,  ${}^{3}T_{1g}(P)$  and  ${}^{3}T_{1g}(F)$ states. But we have found only two of the possible electronic transitions. The absorption band with  $(12820 \text{ cm}^{-1})$ arises lower energy from  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  transition, while the absorption band with higher energy  $(23809 \text{ cm}^{-1})$  corresponds to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$  transition. The positions of the d-d transitions indicate that the Ni ion is in a polymeric octahedral environment with bridging bromides [5]. The magnetic moment value  $(\mu_{\rm eff} = 3.20 \text{ BM})$  of the complex, which shows the presence of two unpaired electrons, lies in the region expected for octahedral Ni complexes [3]. This value is only a little higher than the calculated value for two unpaired electron, which indicates metal-metal interaction is absent, and the discrepancy can be attributed to the contribution made by orbital motion of the electrons [20].

The electronic absorption spectrum of Co(II) complex shows one broad band in visible region at  $14925 \text{ cm}^{-1}$  and gives some shoulders around 15625, 16077 and 16649  $\text{cm}^{-1}$ . The complex is blue in color, which is a characteristic for tetrahedrally coordinated cobalt complexes [21,22]. The band at 14925  $\text{cm}^{-1}$  is a spin allowed electronic transition and arises from  ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$ . The bands at 15625, 16077 and  $16649 \text{ cm}^{-1}$  come from spin forbidden transitions and assignable to  ${}^{4}A_{2}(F) \rightarrow {}^{2}E(G), \, {}^{4}A_{2}(F) \rightarrow {}^{2}T_{1}(G)$  and  ${}^{4}A_{2}(F) \rightarrow {}^{2}T_{2}(G)$ , respectively, indicating fine structures due to pseudo-tetrahedral structure. Holm and Cotton [22] have made an extensive study on magnetic investigation of a number of cobalt complexes. They have reported that cobalt-halide with pmethylaniline (pMA) complexes have a tetrahedral arrangement around cobalt ion and possess magnetic moment values laying in the range 4.80-4.72 BM. We have also found the value of magnetic moment of

391

Table 4

Thermal decomposition	processes of	the metal	complexes
-----------------------	--------------	-----------	-----------

	1 1				
Compound	Process	Temp. range (°C)	DTG peak temp. (°C)	Weight loss (%)	
				Calc.	Found
$[MnBr_2(mMA)_2]_n$	$[MnBr_2(mMA)_2] \rightarrow [MnBr_2(mMA)_{0.4}]$	115-183	178	29.12	26.68
	$[MnBr_2(mMA)_{0.4}] \rightarrow MnBr_2$	183-310	202	19.83	17.78
	$MnBr_2 \rightarrow MnO$	350-750	670	33.39	35.93
[CoBr <sub>2</sub> (mMA) <sub>2</sub> ]	$[CoBr_2(mMA)_2] \rightarrow CoBr_2$	97-350	250	49.40	47.70
	$CoBr_2 \rightarrow CoO$	390-710	690	33.29	36.62
$[NiBr_2(mMA)_2]_n$	$[NiBr_2(mMA)_2] \rightarrow NiBr_2$	90-380	235	50.33	49.31
2. /2	$NiBr_2 \rightarrow NiO$	400-720	685	33.08	34.88



Fig. 5. TG-DTG curves of  $[MnBr_2(mMA)_2]_n$  (sample mass: 8.9907 mg, heating ratio: 10 °C/min, under N<sub>2</sub> atmosphere with a flow rate: 5 ml/min).

 $[CoBr_2(mMA)_2]$  complex as 4.73 BM which falls into that reported region. Hence, the value obtained for magnetic moment proposes that complex has a high spin tetrahedral N<sub>2</sub>CoBr<sub>2</sub> coordination sphere.

### 3.3. Thermal analysis

Thermal decomposition data of the metal complexes are listed in Table 4. As an example, TG and DTG traces for Mn(II) complex are shown in Fig. 5. In the TG-DTG curves of Mn(II) complex no weight changes are observed until 115 °C, where an initial weight loss is observed, due to the loss of 60% mMA molecules. In the temperatures between 183 and 310 °C, the rest of the mMA molecules is removed immediately from the complex, leaving the intermediate MnBr<sub>2</sub>. The metal salt starts to decompose at 350 °C. The residual weight is in good agreement with the value required for MnO.

The Co(II) and Ni(II) complexes decompose in a two-step mass loss reaction. The first step  $(97-350 \text{ }^{\circ}\text{C}$ 

range) for the Co(II) complex corresponds to the loss of 2 mol of mMA. The second decomposition stage registered between 390-710 °C matches the decomposition of CoBr<sub>2</sub> finally to CoO. The Ni(II) complex loses its 49.31% mass in the range 90-380 °C, corresponding to the complete removal of mMA from the complex. The second step in the range 400-720 °C in which the maximum mass loss occurs at 685 °C is the evidence of decomposition of NiBr2 to metal oxide. The observed weight losses for the decomposition processes in each of the compounds compare favorably with the theoretical values listed in Table 4. The initial decomposition temperature of each complex reveals the following thermal stability sequence Mn > Co > Ni which is the inverse order of Irwing–Williams series [20].

## 4. Conclusion

The spectroscopic studies of mMA complexes of some metal bromides show that coordination occurs

via nitrogen atom of the mMA. The IR and Raman spectra reveal the type of the coordination around each metal ion. The information referring to the geometry of the studied complexes is also obtained from the electronic spectra and from values of magnetic moments. Without X-ray analysis, no define structure can be described. However, the spectroscopic and magnetic data suggest that the Co(II) complex has a tetrahedral structure, with the cobalt ion bonded to two bromide ions and two nitrogen atoms from two different molecules of ligand, while the Mn(II) and Ni(II) complexes have the metal ions in a polymeric octahedral environment with bridging bromides. The metal complexes decompose via intermediate complexes to give the metal oxides.

## Acknowledgements

We thank Dr Wolfgang H Meyer for providing research facilities in Max-Planck Institute for Polymer Research, Germany, and Dr Mehmet Somer for Raman measurements in Koc University, Turkey.

## References

[1] K. Verschueren, Handbook of Environmental Data on Organic Chemicals, third ed., van Nostrand, New York, 1996.

- [2] T. Abe, H. Saito, Y. Niikura, T. Shiegeoka, Y. Nakano, Chemoshpere 45 (2001) 487.
- [3] J.R. Allan, A.D. Paton, Thermochim. Acta 214 (1993) 235.
- [4] C. Engelter, D. Thornton, M.R. Ziman, J. Mol. Struct. 49 (1978) 7.
- [5] I.S. Ahuja, D.H. Brown, R.H. Nuttall, D.W.A. Sharp, J. Inorg. Nucl. Chem. 27 (1965) 1625.
- [6] J.A. Lee-Thorp, J.E. Ruede, D.A. Thornton, J. Mol. Struct. 50 (1978) 65.
- [7] M. Kumru, A. Aypar, Spectrochim. Acta Part A 47 (1991) 1789.
- [8] S. Akyuz, J.E.D. Davies, J. Mol. Struct. 95 (1982) 157.
- [9] E. Akalin, S. Akyuz, J. Mol. Struct. 482–483 (1999) 175.
- [10] A. Altun, K. Golcuk, M. Kumru, Vib. Spectrosc. 31 (2003)
- 215.[11] K. Golcuk, A. Altun, M. Kumru, Spectrochim. Acta Part A 59 (2003) 1841.
- [12] K. Golcuk, A. Altun, S. Guner, M. Kumru, B. Aktas, Spectrochim. Acta, Part A (2003) in press.
- [13] A. Altun, K. Golcuk, M. Kumru, J. Mol. Struct. (Theochem) 625 (1–3) (2003) 17.
- [14] M.A.J. Jungbauer, C. Curran, Spectrochim. Acta 21 (1965) 641.
- [15] S. Yurdakul, A.I. Sen, Vib. Spectrosc. 20 (1999) 27.
- [16] R.J.H. Clark, C.S. Williams, Inorg. Chem. 4 (1965) 350.
- [17] S.P. Perlepes, S. Kasselouri, A. Garoufis, F. Lutz, R. Bau, Polyhedron 14 (11) (1995) 1461.
- [18] L.P. le Roux, A.M. Heyns, J. Mol. Struct. 406 (1997) 75.
- [19] L. David, M. Rusu, O. Cozar, D. Rusu, M. Todica, C. Balan, J. Mol. Struct. 482 (1999) 149.
- [20] F.A. Cotton, G. Wilkonson, P.L. Gaus, Basic Inorg. Chem., Wiley, New York, 1995.
- [21] J.R. Allan, D.H. Brown, R.H. Nuttall, D.W.A. Sharp, J. Inorg. Nucl. Chem. 26 (1964) 1895.
- [22] R.H. Holm, F.A. Cotton, J. Chem. Phy. 32 (4) (1960) 1168.

393