HACETTEPE JOURNAL OF BIOLOGY AND CHEMISTRY
Research Article
Hacettepe J. Biol. & Chem., 2008, 36(1), 31-39

Synthesis of the 4-N,N-Dimethylaminobenzoic Acid Complexes of Mn(II), Co(II), Ni(II), and Cu(II). Spectroscopic and Thermal Characterization

Özgür Aybirdi[1], Dursun Ali Köse[1,2]*, Hacali Necefoglu[1]

[1]Kafkas University, Faculty of Sciences & Arts, Department of Chemistry, Kars, Turkey

[2]Department of Chemistry, Hacettepe University, Beytepe, 06532 Ankara, Turkey

Abstract

4-N,N-dimethylaminobenzoic acid complexes of Mn(II), Co(II), Ni(II) and Cu(II) were synthesised and their structural properties were investigated by employing elemental analysis, magnetic susceptibilitiy, solid state UV-vis, direct injection probe mass, FTIR and thermoanalytic TG-DTG methods. According to the microanalytical results, formula of complexes are $C_{18}H_{32}N_2O_{10}Mn$, $C_{18}H_{24}N_2O_6Co$, $C_{18}H_{34}N_2O_{11}Ni$ and $C_{18}H_{24}N_2O_6Cu$. The complexes of Mn(II) and Ni(II) contain four moles of coordination waters, but Co(II) and Cu(II) complexes have two moles of coordinated water ligands. All of the complexes include two moles 4-N,N-dimethylaminobenzoate ligands, but it was coordinated to metal atom as monodentate in Mn(II) and Ni(II) and bidentate in Co(II) and Cu(II) complexes. It was found that ratio of metal:ligand is 1:2 and the decomposition of each complex starts with dehydration and follows by decomposition of organic part, respectively. The thermal dehydration of the complexes takes place in steps from one to two. The decomposition mechanism and thermal stability of the investigated complexes are interpreted in terms of their structures. The final decomposition products are found to be the respective metal oxides.

Key Words: 4-N,N-dimethylaminobenzoate; thermal decomposition; metal complexes; transition metal compounds.

INTRODUCTION

The carboxylates play an important role in inorganic chemistry and bioinorganic chemistry, and many metal cations in a great number of various biological processes, especially six-membered ring system, are components of several vitamins and drugs [1]. 4-*N,N*-dimethylaminobenzoic acid or *p*-dimethylamino benzoic acid (4-dmaba) is a derivative of benzoic acid. The harmfull effects of sunbeams are prevented or minimized by 4-*N,N*-dimethylamino benzoic acid so it is very important material in cosmetic industry. The 4-dmaba and its co-polymers absorb ultra violet beams [2]. Especially metal salts or complexes of 4-*N,N*-dimethylaminobenzoic acid are used to cosmetic industry. Aluminium complex of 4-dmaba is a material of cosmetic because it is hydrophobic and stable of towards to conditions of environment [3]. On the other hand, the salts of Mg, Ca, Zn and Zr are used to in dyes of cosmetic products as supplement material [4,5]. The zinc

---

* Correspondence to: Dursun Ali Köse

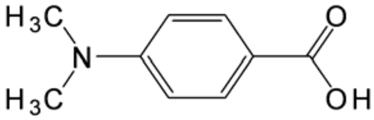
Hacettepe University; Department of Chemistry, Ankara, Turkey

Tel: +90 312 297 79 94 Fax: +90 312 299 21 63
E-mail: dkose@hacettepe.edu.tr

complex of 4-dmaba is effective towards to hepatit C virus, so it was investigated as anti-virus drug towards to hepatit C by Otsuka Medicine Company [6]. On the other hand, 4-dmaba and metal salts are used as charge-transfer agent with various organic molecules [7-13]. The some metal complexes of 4-dmaba activate to formation of polymeric structure preventive to sunbeams [14]. Separately, the titanium complex of 4-dmaba was used to for production of liquid resin that durable against to heat [15]. The studies on mixed-ligand complex formation have also a great deal of importance in the field of biological and environmental chemistry.

In this work, Mn(II), Co(II), Ni(II), and Cu(II) with 4-*N,N*-dimethylaminobenzoic acid complexes have been synthesised and their thermal decomposition results have been presented. The decomposition pathways of the investigated complexes are discussed in connection with the available spectroscopic data.

EXPERIMENTAL



4-dmaba

Scheme 1.

Materials and instrumentation

All chemicals were used analytical reagent products. $MnSO_4.H_2O$, $CoSO_4.7H_2O$, $NiSO_4.6H_2O$, $CuSO_4.5H_2O$ and 4-*N,N*-dimethylaminobenzoic acid were obtained from Merck (Darmstadt, Germany). Elemental analysis (C,H,N) were carried out by standard methods (Tubitak Marmara Research Center). Magnetic susceptibility measurements were performed at room temperatures using a Sherwood Scientific MXI model Gouy magnetic balance. IR spectra was recorded in the 4000-400 cm^{-1} region with a Perkin Elmer 1000 FT-IR spectrophotometer using KBr pellets. Thermal analysis curves (TG-DTA) were recorded simultaneously in a static air atmosphere with a Schimadzu DTG 60 thermal analyzer. The samples weighed approximately 10 mg and highly sintered a-Al_2O_3 was used as a reference material. The heating rate was 10°C min^{-1} and the DTG sensitivity was 0.05 mg s^{-1}. We used a Schimadzu UV3600/UV-VIS-NIR model spectrophotometer for solid state ultraviolet-visible range studies. Mass spectrum data was recorded Agilent Technologies 5973 spectrophotometer using DIP-MS method.

Preparation of 4-*N,N*-dimethylaminobenzoate complexes

In the first step, sodium salt of 4-*N,N*-dimethylamino benzoic acid was prepared, and metal 4-*N,N*-dimethylaminobenzoic complexes were synthesized used to substation reaction. The $M(4\text{-dmaba})_2.nH_2O$ solution was allowed two weeks for crystallization at room temperature. The crystals formed were filtered and washed with cold water and acetone and dried in vacuo.

$C_{18}H_{32}N_2O_{10}Mn$ (491.40); C 43.87 (44.00); H 6.05 (6.56); N 5.68 (5.70).
$C_{18}H_{24}N_2O_6Co$ (423.33); C 51.29 (51.94); H 5.23 (5.71); N 6.56 (6.62).
$C_{18}H_{34}N_2O_{11}Ni$ (513.16); C 41.97 (42.13); H 6.26 (6.68); N 5.35 (5.46).
$C_{18}H_{24}N_2O_6Cu$ (427.95); C 50.07 (50.52); H 5.19 (5.65); N 6.43 (6.55).

RESULT AND DISCUSSION

The results of the elemental analysis indicated that the complexes contain two moles of 4-*N,N*-

Table 1. Characteristic data of the metal complexes.

Complex	M (g/mol)	Yield (%)	Color	d.p.a(˚C)	μ_{eff}
$[Mn(4\text{-}dmaba)_2(H_2O)_4].2H_2O$	491.40	91	pale-yellow	44	5.92
$[Co(4\text{-}dmaba)_2(H_2O)_2]$	423.33	93	pink	64	4.54
$[Ni(4\text{-}dmaba)_2(H_2O)_4].3H_2O$	513.16	87	green	67	2.93
$[Cu(4\text{-}dmaba)_2(H_2O)_2]$	427.95	83	pale-green	60	1.67

[a] decomposition point

dimethylaminobenzoate ligands per mole formula unit. Effective magnetic moments and compositions of the complexes are given in Table 1 in accord with literature values for similar complexes [16-18].

All of the complexes may be thought octahedral coordination around the metal ions. The octahedral coordination of the Ni(II) and Mn(II) ions are completed by two acidic oxygen atoms of carboxylate group from two 4-dmaba [19]. The coordination sphere of Co(II) and Cu(II) are octahedral structure that was completed by acidic oxygen and carboxyl oxygen of carboxylate group from two 4-dmaba. Octahedral structure are confirmed by magnetic data. All of the complexes contain two moles of aqua ligand that are directly coordinated to metal ion. According to the magnetic susceptibility results, the metal complexes are paramagnetic and magnetic susceptibility data were given at Table 1. The results are compatible to literature. Due to the low solubility of the complexes, the electronic spectrum of the structures were taken in the solid state. The electronic spectra showed two absorption bands and d–d transition at 7100 cm^{-1} ($^4T_{1g}\rightarrow{}^4T_{2g}$) and 20230 cm^{-1} ($^4T_{1g}\rightarrow{}^4T_{1g}$)($^4P$) for Co(II) complex; three absorption bands and d–d transition at 7680 cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{2g}$), 15350 cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{1g}$)($^3F$), and 25050cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{1g}$)($^3P$) for Ni(II) complex respectively. In the Cu(II) complex is observed multiple absorbsition band at about 11200cm^{-1} – 16700 cm^{-1} but they are overlapped. Because, octahedral complexes of Cu(II) are observable distorted by Jahn-Teller effect and the structure of complex is to name pseudo-octahedral. It was to taken notice of top of the peak as absorption band and d–d transition at about 13360 cm^{-1} ($^2E_g\rightarrow{}^2T_{2g}$) for Cu(II) complex. The UV-visible peaks corresponding to the the $p\rightarrow p^*$ transitions in the ligands were observed at 270 and 320 nm [20,21]. The peaks belonging to the $p\rightarrow p^*$ transitions are shifted to a longer wawelength as a consequence of coordination when binding with metal, confirming the formation of 4-dmaba metal complexes.

FT-IR spectra

Characteristic FT-IR peaks of the complexes are given in Table 2. The absorption bands at the range of 3650–2900 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of water molecules. The main difference in the spectrum of 4-dmaba is that the C=O stretching vibration of the carboxyl group at 1720 cm^{-1} shifts to lower frequency in all the metal complexes. The complexes give rise to strong bands responsible from the C=O stretching at 1619 cm^{-1} in Mn(II) complex and 1617 cm^{-1} in Ni(II) complex. These structures are contain monodentate 4-dmaba ligand. The complexes of Co(II) and Cu(II) give rise strong bands at 1595 cm^{-1} and 1596 cm^{-1}, respectively. The shifts to lower frequency of the C=O peaks in Co(II) and Cu(II) complexes according to Mn(II) and Ni(II)

Table 2. Some selected characteristic FT-IR peaks of metal complexes

Groups	Mn(II)	Co(II)	Ni(II)	Cu(II)
n(-OH)$_{\text{Water}}$	3650-3050	3600-3100	3550-2900	3650-3150
n(C=O)$_{\text{carboxy}}$	1609	1604	1607	1603
n(COO$^-$)$_{\text{as}}$	1571	1524	1572	1528
n(COO$^-$)$_{\text{s}}$	1388	1395	1387	1396
∆n	183	129	185	132
n(C-O-C)	1191	1188	1189	1190
n(C-H)	1356	1358	1362	1364
d(C-H)	2825	2809	2819	2813
n(C-N)	1232	1276	1232	1287
n(C=C)$_{\text{ring}}$	1664	1659	1673	1671
n(C-C)$_{\text{ring}}$	1128	1133	1129	1137
n(Me-O)	598	605	598	616

complexes indicated that bidentate coordination. This shows that the coordination takes place through the carboxyl group [22-24]. The low intensity bands in the region of 616–598 cm^{-1} are attributed to M–O vibration [25].

Thermal Analysis

The thermoanalytical curves of the studied complexes are shown in Figure 1. The corresponding thermal decomposition data are summarized in Table 3.

$[Mn(C_9H_{10}NO_2)_2(H_2O)_4].2H_2O$

The Mn(II) complex starts to decomposition at 35°C with removing of water molecules. The two moles hyrated and four moles coordinated waters are eliminated in a single step accompanied by a single endothermic DTA peak at 68°C (Figure 1a) (exp. 20.14%; calcd. 21.90%). In the second stage, two moles of 4-*N,N*-dimethylaminobenzoate ligands are lost in four consecutive steps (DTG peaks at 255, 410, 498 and 712°C). While, the decomposition peak at 255°C is exothermic, others are endothermic. There is a good agreement between the experimental and calculated values for the mass loss (exp. 66.12%; calcd. 66.83%). In the following step, remained decompotion product is MnO (exp. 13.74%; calcd. 14.36%).

$[Co(C_9H_{10}NO_2)_2(H_2O)_2]$

The thermal analysis curves of the complex were shown in Figure 1b. The elimination of the water molecules occurs between 45 and 115°C and the DTA curve shows an endothermic effect at 66°C indicating the formation of the anhydrous complex (exp. 7.68%; calcd. 8.49%). The anhydrous complex is stable up to 196°C and reveals a 78.48% (calcd. 77.57%) mass loss between 196-591°C corresponding to the release of the two moles of 4-*N,N*-dimethylaminobenzoate ligands. In this temperature range, decomposition shows four DTG peaks at 211°C (endothermic) and 371, 410, 435°C (exothermic). Finally, the trial product was found to be CoO (exp. 15.24%; calcd. 16.75%).

$[Ni(C_9H_{10}NO_2)_2(H_2O)_4].3H_2O$

The first step in the decomposition corresponds to the dehydration of the complex (Figure 1c). The endotherm observed at 85°C corresponds to the dehydration and indicates that water molecules are coordinated to metal ion and hydrated waters (exp.

23.65%; calcd. 24.55%). The anhydrous complex exists in the 112-228°C temperature interval. During the second stage, the anhydrous complex begins to decompose at 147°C with melting (DTA curve).

The following steps involves the consecutive decomposition of the two moles of 4-*N,N*-dimethylaminobenzoate ligands in the temperature range of 228-816°C (exp. 61.36%; calcd. 63.99%).

In this temperature range, decomposition shows three DTG peaks at 264°C (endothermic) and 379, 719°C (exothermic). NiO is found to be final decomposition product (exp. 15.35%; calcd. 13.56%).

$[Cu(C_9H_{10}NO_2)_2(H_2O)_2]$

The thermal dehydration of this complex occurs in one step (Fig.1d). In the first stage of the decomposition, two moles of aqua ligand is removed in the temperature range of 53-118°C (exp. 7.84%; calcd. 8.41%). After the dehydration, the anhydrous complex, $[Cu(C_9H_{10}NO_2)_2]$ is stable in the temperature of 119-189°C. At the 242 (endothermic), 537 and 685°C (exothermic) DTA peaks two moles of organic ligands decompose in the temperature range of 189–838°C (exp. 75.18%; calc. 76.73%). At the result of the removing ligands produced CuO (exp. 16.98%; calc. 18.55%).

Mass spectra

To conclude the thermal decomposition pathway of the [Ni(*4-dmaba*)$_2$(H_2O)$_4$].3H_2O complex mass spectrum was recorded (Fig. 2) using direct insertion probe pyrolysis mass spectrometry method. The molecular ion peak is detected at 512 m/z in the mass spectrum recorded. The obtained mass spectrum is relatively complex and exhibits a large number of peaks that extend to *m/z*. Beside the

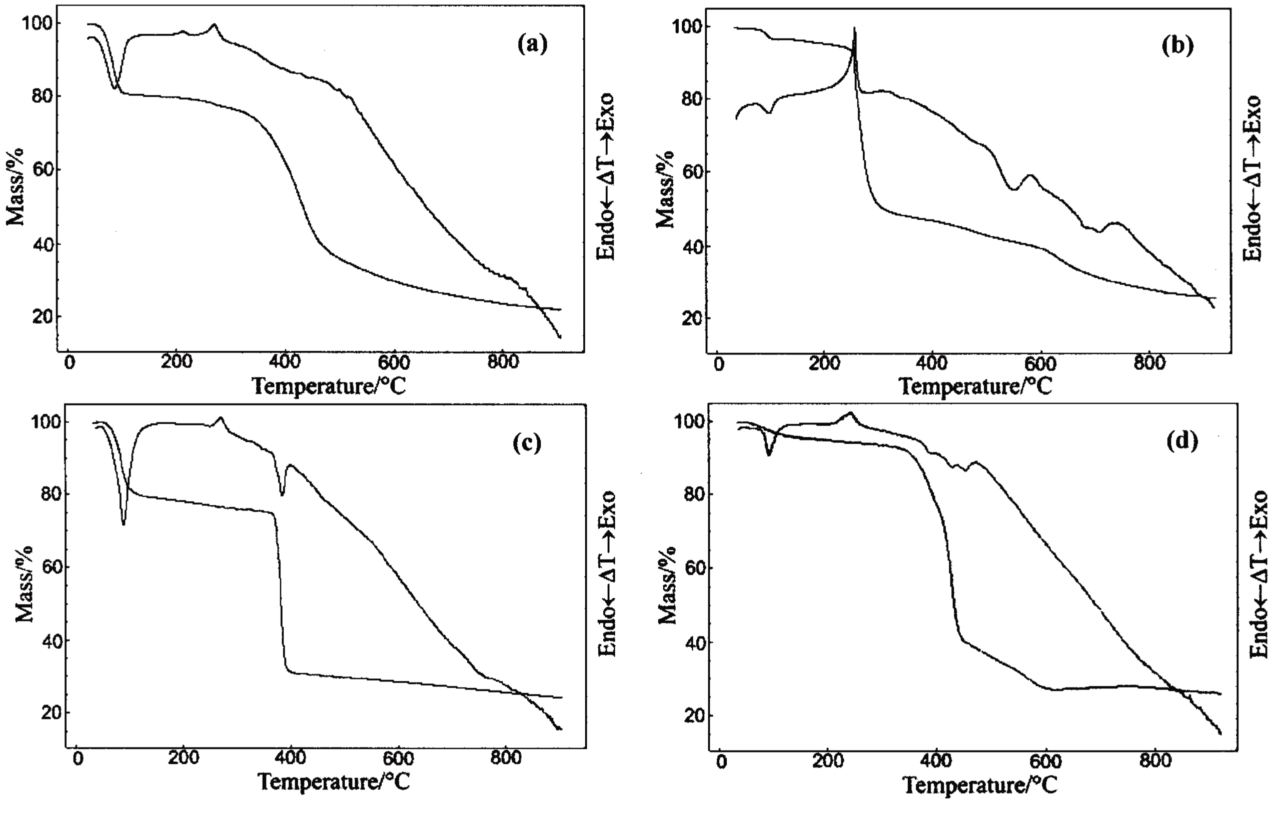


Figure.1. TG-DTA curves of the complexes: (a) [Mn(4-dmaba)$_2$(H_2O)$_4$].2H_2O; (b) [Co(4-dmaba)$_2$(H_2O)$_2$]; (c) [Ni(4-dmaba)$_2$(H_2O)$_4$].3H_2O, and (d) [Cu(4-dmaba)$_2$(H_2O)$_2$]

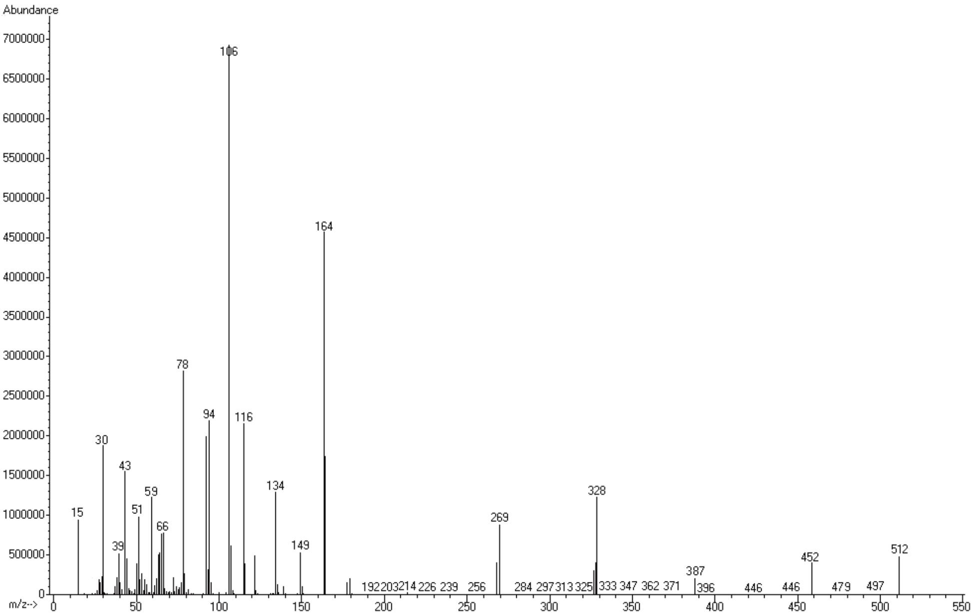


Figure.2. Mass spectrum of [Ni(*4-dmaba*)$_2$(H_2O)$_4$].3H_2O complex.

most abundant peaks, much fewer abundant peaks observed on the spectrum depend probably on the nature of ligands. These peaks are belong to decomposition products of complex and ligands. The mass spectrum shows the fragmentation pattern and the most fragile points of the molecule.

CONCLUSION

The thermal decomposition of the investigated complexes takes place in two steps: dehydration, the elimination of 4-*N,N*-dimethylaminobenzoate ligands. Regardless of the coordination, the decomposition of the complexes starts with dehydration process.

While, the complexes of Mn(II) and Ni(II) ions contain hydrate water, complexes of Co(II) and Cu(II) ions do not. This behaviour was also observed in our early studies [25]. All the dehydration and decomposition data of complexes are presented in Table 3. The complexes of Co(II) and Cu(II) ions have two moles of coordinated water, but Mn(II) and Ni(II) complexes have four moles of coordinated water ligands. As result of this, 4-dmaba ligand bonds to metal ion with bidentate coordination in Co(II) and Cu(II) complexes by using carboxyl oxygen and ionic acidic oxygen and monodentate coordination in Mn(II) and Ni(II) complexes by using only ionic acidic oxygen atom. There is a study about determination of [Mn(*4-dmaba*)$_2$(H_2O)$_4$].2H_2O structure in literature (Figure 3) [16] that is support suggested structures by us. In the course of the removing of 4-dmaba ligand occurs that one from decomposition steps give an exothermic peak at 255, 211, 264 and 242°C, respectively. The other peaks are endothermic. This result may be concern to burning of metil groups in all of the structures. The thermal stability of hydrated complexes follows the order:

Ni(II)	>	Cu(II)	>	Mn(II)	>	Co(II)
85°C		82°C		68°C		60°C

The final decomposition products were found to be the respective metal oxides formed in the 600–900°C temperature intervals that compatible with literature [26,27].

While, in the Co(II) and Cu(II) complexes, suggested that, 4-dmaba ligands are coordinated to the metal ion as bidendate, 4-dmaba ligands coordinate as monodentate in the Mn(II) and Ni(II) complexes. The IR spectra of the intermediate products showed similar results. The $(COO^{-})_{asym.}$ peaks are located at 1571 cm^{-1} for Mn(II), 1524 cm^{-1} for Co(II), 1572 cm^{-1} for Ni(II) and 1528 cm^{-1} for Cu(II) complexes. $(COO^{-})_{sym.}$ peaks are observed at 1388 cm^{-1} for Mn(II), 1395 cm^{-1} for Co(II), 1387 cm^{-1} for Ni(II) and 1396 cm^{-1} for Cu(II) complexes. The shifts (D) between of the $n_{asym.}$ and $n_{sym.}$ bands of COO^{-} groups for Mn(II) and Ni(II) are 183 and 185 cm^{-1}, repectively and more than for the sodium salt 4-*N,N*-dimethylaminobenzoic acid (163 cm^{-1}) that support monodentate carboxylate group exist. But, the shifts (D) between of the $n_{asym.}$ and $n_{sym.}$ bands of COO^{-} groups for Co(II) and Cu(II) are 129 and 132 cm^{-1}, repectively and less than for the sodium salt 4-*N,N*-dimethylaminobenzoic acid (163cm^{-1}) that support bidentate carboxylate group exist [16-18,26-31].

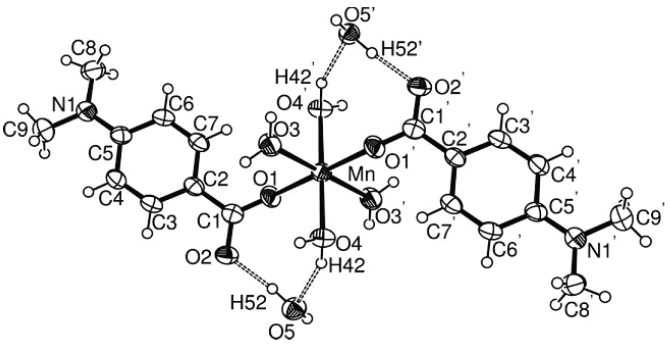
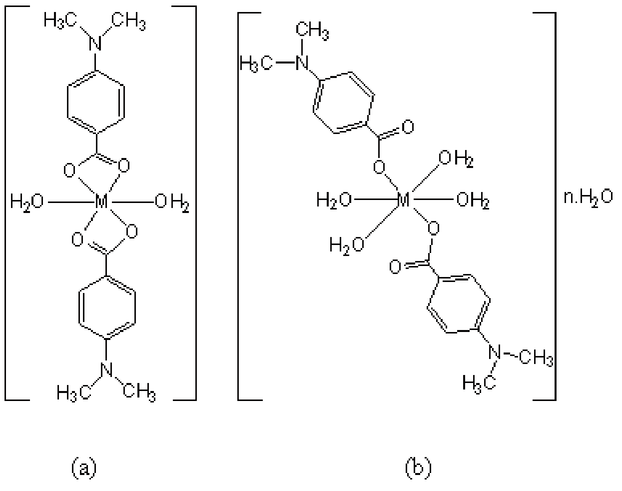


Figure 3. The structure of $[Mn(4\text{-}dmaba)_2(H_2O)_4].2H_2O$ in literature [16].



(a) (b)

Figure 4. (a) Suggested structure for Co(II) and Cu(II) complexes. (b) Suggested structure for Mn(II) and Ni(II) complexes.

The structures of the synthesized complexes, which are presented in Figure 4, are consistent with their chemical, thermal and spectroscopic properties.

REFERENCES

1. W. Ferenc, B. Cristovao, B. Mazurek and J. Sarzynski, Journal of the Serbian Chemical Society 71(8-9) (2006) 929.
2. D. Baiiley, D. Tirrell, O. Vogl., J. Macromol. Sci., Chem., A12(5) (1978) 661.
3. J.B. Randal, L.L. Melvin, W.K. James, (Stepan Co.) Eur. Pat. Appl. EP 220,934 (Cl. C07F5/06), 06 May 1987, US Appl. 790,486, 23 Oct 1985 p.49.
4. Kanebo Ltd, Jpn. Kokai Tokyo Koho Jp 60,130,654 [85,130,654] (Cl. C09C3/08), 12 Jul 1985, Appl. 83/240,031, 19 Dec 1983; 9.

5 Kanebo Ltd. Jpn. Kokai Tokyo Koho JP 60,94,949[85,94,949] (Cl.C07C101/60), 28 May 1985, Appl. 83/203,539, 29 Oct 1983, 6

6 Mori, Makoto (Otsuka Pharmaceutical Co., Ltd.; Mori, Masamoto; Nagamine, Takeaki; Kuboki, Makoto, Japan) PCT Int. Appl. WO 96 41,643 (Cl.A61K38/21), 27 Dec 1996, JP Appl. 96/51,784, 8 Mar 1996; 25.

7. Kysel O., Z. Phys. Chem., 89(1-4) (1974) p.62.
8. K.Y. Hee, C.D. Won, Y. Minjoong, K. Dongho., J. Photosci., 3(3) (1996) 153.
9. Y.B. Jiang, X.J. Wang M.G.Jin, L.R. Lin, J.Photochem. Photobio., A126(1-3), (1999) 125.
10. Y.B. Jiang, Chinese. Sci. Bull., 39(14) (1994) 1179.
11. Y.H. Kim, D.W. Cho, M. Yoon D. Kim, J. Phys. Chem., 100(39) (1996) 15670.
12. M. Yoon, D.P.S Negi., Proc. Indian Acad. Sci.-Chem. Sci., 114(6) (2002) 593.
13. T. Gunnlaugsson, A.J. Harte; J.P. Leonard, M. Nieuwenhuyzen, Supramol. Chem., 15(7-8) (2003) 505.
14. J. Rawlings; C.A.L. Mahaffy, Spectrosc. Lett., 21(7) (1988) 597.

15. J.M. Salvatore, G.Sugerman (Kenrich Petrochemicals, Inc.) Ger. Offen. 2,703,829 (Cl. C08K5/56), 04 Aug 1977, US Appl. 653,773, 30 Jan 1976, 3
16. T. Hökelek and H. Necefoglu, Acta Cryst., E63 (2007) 821.
17. D.A. Kose, MSc. Thesis, Univ. Kafkas (2001).
18. Ö. Aybirdi, MSc. Thesis, Univ. Kafkas (2001).
19. D.A. Köse, Russ. J. Inorg. Chem., 52(9) (2007) 1384.
20. H. Icbudak, H. Olmez, O.Z. Yesilel, F. Arslan, P. Naumov, G. Jovanovski, A.R. Ibrahim, A. Usman, H.K. Fun, S. Chantrapromma and S.W. Ng, J. Mol. Struct., 6572 (2003) 55.
21. D.A. Köse, B. Zümreoglu-Karan, O. Şahin and O. Büyükgüngör, J. Mol. Struct., 789(1-3) (2006) 147.
22. D.A. Köse, B. Zümreoglu-Karan, C. Unaleroğlu, O. Şahin and O. Büyükgüngör, J. Coord. Chem., 18 (2006) 2125.
23. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley and Sons, New York, (1978) 197.
24. J. Zsakó, G. Pokol, Cs. Novák, Cs. Várhelyi, A. Dobó and G. Liptay, J. Therm. Anal. Cal., 64, (2001) 843.
25. H. Icbudak, Z. Heren, D.A. Kose and H. Necefoglu, J. Therm. Anal.Cal., 76 (2004) 837.
26. W. Ferenc and A.W. Dziewulska, J. Therm. Analys. Cal., 71 (2000) 923.
27. W. Ferenc, B. Cristovao, and J. Sarzynski, J. Therm. Analys. Cal., 86(3) (2006) 783.
28. D.A. Köse, E.F. Öztürkkan, H. Necefoğlu, İ. Uzun, Assian J. Chem., 19(6) (2007) 4880.
29. D.A. Köse, A. Kaya, H. Necefoğlu, Russ. J. Coord. Chem., 33(6) (2007) 422.
30. D.A.Köse, H. İçbudak and H. Necefoğlu, Hacettepe J. Biol. & Chem., 35(2) (2007) 123.
31. D.A. Köse, B. Zümreoglu-Karan, B. Koşar and O. Büyükgüngör, J. Chem. Cryst. (Online published 4 December 2007).

Table 3. Thermal analysis data of metal complexes.

Complex		*Temp. Range(°C)*	*Max.Dec.Temp. (°C) DTG max.*	*Remove Group*	*Weight Loss (%) Exp.—Calc.*	*Total Weight Loss (%) Exp.—Calc.*	*Decomposition Product*	*Colour*
$[Mn(C_9H_{10}NO_2)_2(H_2O)_4].2H_2O$ M.A=491.40								pale-yellow
	1	35 – 101	68(+)	$6H_2O$	20.14 – 21.90		$[Mn(C_9H_{10}NO_2)_2]$	
	2 3	240 – 296 301 – 864	255(−) 410(+) 498(+) 712(+)	$2(C_9H_{10}NO_2)$	3.79 62.33 } – 66.83			
						86.26 — 85.64	MnO	dark-green
$[Co(C_9H_{10}NO_2)_2(H_2O)_2]$ M.A=423.33								pink
	1	45 – 115	66(+)	$2H_2O$	7.68–8.49		$[Co(C_9H_{10}NO_2)_2]$	
	2 3 4 5	196–241 294–383 384–431 432–591	211(−) 371(+) 410(+) 435(+)	$2(C_9H_{10}NO_2)$	18.48 44.07 } – 77.57 15.48			
						84.76 – 83.25	CoO	black-grey
$[Ni(C_9H_{10}NO_2)_2(H_2O)_4].3H_2O$ M.A=513.16								light-green
	1	49 – 111	85(+)	$7H_2O$	23.65 – 24.55		$[Ni(C_9H_{10}NO_2)_2]$	
	2 3 4	228 – 351 353 – 431 435 – 816	264(−) 379(+) 719(+)	$2(C_9H_{10}NO_2)$	2.62 51.93 } – 63.99 6.81			
						84.65 – 86,44	NiO	black-yellow
$[Cu(C_9H_{10}NO_2)_2(H_2O)_2]$ M.A=427.95								blue
	1	53 – 118	82(+)	$2H_2O$	7.84 – 8.41		$[Cu(C_9H_{10}NO_2)_2]$	
	2 3 4	189 – 308 317 – 586 588 – 838	242(−) 537(+) 685(+)	$2(C_9H_{10}NO_2)$	52.15 10.37 } – 76.73 12.66			
						83.02 – 18.59	CuO	black