

PHYSICO-CHEMICAL CHARACTERIZATION OF MIXED-LIGAND COMPLEXES OF Mn(III) BASED ON THE ACETYLACETONATE AND MALEIC ACID AND ITS HYDROXYLAMINE DERIVATIVE

Suzana M. Cakić, Goran S. Nikolić,
Jakov V. Stamenković and Sandra S. Konstantinović

Two new Mn(III) mixed-ligand complexes with two acetylacetonate (acac) ligands and one maleate ligand and its hydroxylamine derivative of the general formula $[Mn(C_5H_7O_2)_2L]$ were prepared. Their structure was established by using elemental analysis, FTIR and UV/VIS spectroscopic methods, as well as magnetic measurement. Replacement of the acetylacetonate ligand by the corresponding acid ligand has been confirmed in Mn(III) acetylacetonate. Based on the obtained experimental data and literature indications, structural formulae to these compounds were assigned.

KEYWORDS: Mn(III) complexes; maleate and hydroxylaminmaleate ligand; physico-chemical characterization

INTRODUCTION

Complexes of Mn(III) with acetylacetonate and acid residue ligands are of interest not only theoretically but also from a practical point of view. They have found application as selective catalysts for isocyanate-polyol reaction while they could not be used as catalyst for isocyanate-water reaction (1,2,3) in two component water-borne polyurethane coatings.

The interest in this class of compounds as catalyst started in 1973, when the first compounds of this type were synthesized and studied (4).

The variation of metal chelates based ligands can change physico-chemical characteristics of the chelates. It also can yield complexes with different properties compared comparing to the ligands themselves. This also implies the synthesis and investigation of new catalysts (5,6).

Dr. Suzana M. Cakić, Assist., Dr. Goran S. Nikolić, Assist. Prof., Dr. Jakov V. Stamenković, Prof., M.Sc. Sandra S. Konstantinović, Assist., University of Niš, Faculty of Technology, Bulevar Oslobođenja 124, 16000 Leskovac, Serbia and Montenegro, e-mail: suza967@yahoo.com

Synthetic complexes of Mn(III) with mixed ligands based on maleic acid and its hydroxylamine derivatives showed an increased selectivity for the isocyanate/polyol reaction by water-borne two-component polyurethane systems (7,8,9).

This work describes the synthesis of manganese complexes by replacement of acetylacetonate ligand with the corresponding acid ligand as their spectral characteristics.

EXPERIMENTAL

Reagents

All chemicals used were p.a. grade purity. The starting complex $[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3]$ was obtained from commercial sources and was used without further purification.

Synthesis of complexes

Synthesis of Mn(III)-bis(acetylacetonato)maleate (I). Maleic anhydride and methanol (1:1) were refluxed for 120 min. The $[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3]$ was dissolved in benzene. The reaction mixture was cooled and equimolar amounts of $[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3]$ and monomethylmaleate (MMM) were mixed. The mixture was held at 10-25 °C for about 10-20 min. The dark-green product (insoluble in benzene) was filtered under vacuo, washed with solvent and dried at room temperature. The yield was 90%.

Synthesis of Mn(III)-bis(acetylacetonato)hydroxylaminmaleate (II). For the synthesis of this complexes maleic anhydride and methanol (1:1) were refluxed for 120 min, and hydroxylamine hydrochloride in ethanol (0.5 mol dm⁻³) was added in an equimolar amount. The refluxing lasted about 15 min. To cooled redistilled solution, Mn(III) acetylacetonate complex (previously dissolved in a minimal volume of benzene) was added. The green product was filtered under vacuo, washed with solvent and dried at room temperature. The yield was 80%.

Measurements and applied methods

Elemental analyses (C,H,N) were carried out by standard micromethods in the Center for Instrumental Analysis, Faculty of Chemistry, Belgrade.

The Mn content was determined by spectrophotometric method at 525 nm.

The Fourier-transform infrared (FTIR) spectra were recorded using a Michaelson Bomem MB-series spectrophotometer and KBr pellet (1 mg/100 mg) technique. The electronic spectra (UV/VIS) were recorded on a Varian Cary-100 spectrophotometer using 10⁻⁴ mol dm⁻³ solutions in ethanol. Magnetic susceptibilities were determined at room temperature using an MSB-MKI magnetic susceptibility balance (Sherwood Scientific Ltd., Cambridge, England).

RESULTS AND DISCUSSION

The results of microanalysis of carbon, hydrogen and nitrogen in the investigated compounds are given in Table 1. The complexes were synthesized using Mn(III) acetylaceto-

nate and acid ligand in a 1:1 mole ratio. The results in Table 1 indicate replacement of the acetylacetonate ligand by the corresponding acid ligand. The complexes are soluble in H₂O, tetrahydrofuran, propylene glycol, methoxypropylacetate and other polar solvents.

Table 1. Data of elemental analysis of the investigated compounds

Comp.	Mol. Formula	Yield %	Colour	C (%) found (Calcd)	H (%) found (Calcd)	N (%) found (Calcd)	Mn (%) found (Calcd)
I	[Mn(C ₅ H ₇ O ₂) ₂ L ¹⁺]	90	dark-green	44.33 (45.61)	4.57 (4.62)	-	15.3 (14.9)
II	[Mn(C ₅ H ₇ O ₂) ₂ L ²⁺]	80	green	42.51 (43.82)	4.59 (4.70)	3.51 (3.65)	13.6 (14.3)

Infrared spectra

The band at ~3564 cm⁻¹ (-OH stretching vibration) indicates the acetylacetonato ligand replacement with maleic acid in compound (I). The bands at 1708 cm⁻¹ and ~1338 cm⁻¹ have been assigned to the asymmetric and symmetric stretching vibrations of the COOH-group (10). Two bands of the ionized carboxylic group: first at 1615 cm⁻¹ of the asymmetric vibrations and second at 1458 cm⁻¹ from the symmetric vibrations were detected too (Fig. 1).

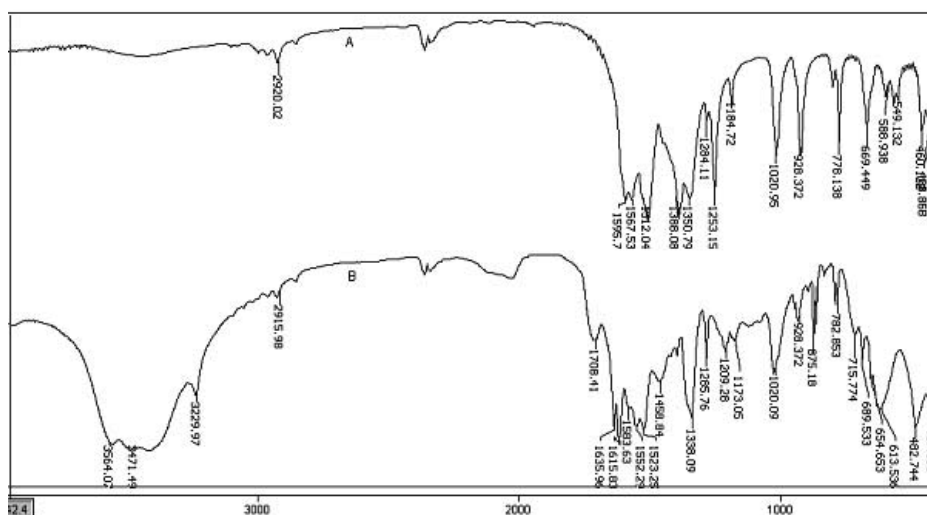


Fig. 1. FTIR spectra: A) - complex of Mn(III) acetylacetonate
B) - complex of Mn(III)-bis(acetylacetonato)maleate

The complex with hydroxylamine derivative of maleic acid showed only vibrations of the $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ at 1595 cm^{-1} and 1407 cm^{-1} .

The bands at $417, 482, 613, 654, 689\text{ cm}^{-1}$, assigned to Mn-O vibrations, as well as, the bands at 928 and 1020 cm^{-1} show that Mn(III) is bonded to two acetylacetonato ligands. A band at 1312 cm^{-1} assigned to coupling of the $\nu(\text{C-N})$ and $\delta(\text{N-H})$ vibrations and $\delta(\text{N-H})$ deformation band at 717 cm^{-1} confirms this suggestion (Table II).

In the complex (II) two major bands appeared: NH stretching vibrations at $\sim 3559\text{ cm}^{-1}$ and the band assigned to the vibration of the carbonyl C=O group (1651 cm^{-1}) indicating replacement of the acetylacetonato ligand with hydroxylaminmaleate ligand (11, 12).

The bands at $417, 482, 613, 654, 689\text{ cm}^{-1}$, assigned to Mn-O vibrations, as well as, bands at 927 and 1023 cm^{-1} show that Mn(III) is coordinated to two acetylacetonato ligands (Fig. 2).

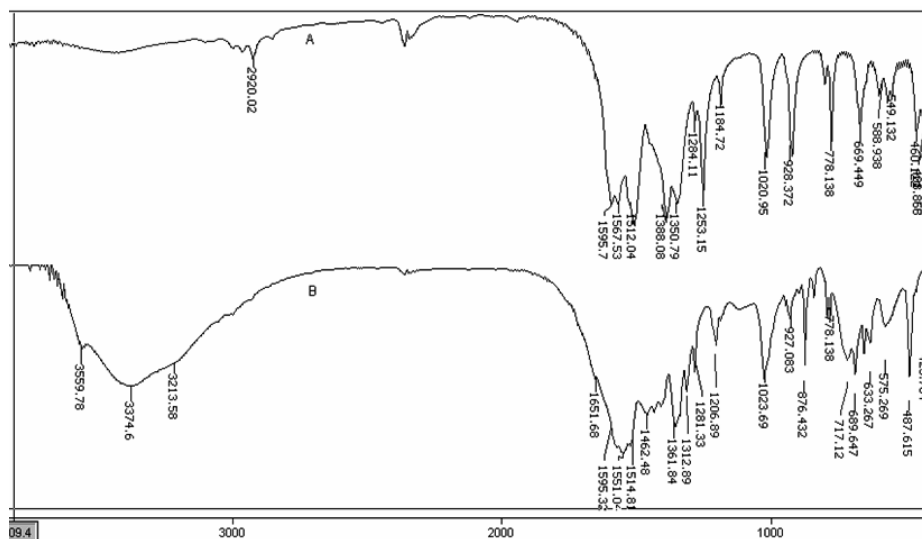


Fig. 2. FTIR spectra: A) - complex of Mn(III) acetylacetonate
B) - complex of Mn(III)-bis(acetylacetonato)hydroxylaminmaleate

The main frequencies and their assignments are presented in Table 2.

Thus, data (Table 2) from the infrared spectra provide clear evidence that the ligands of maleic acid and its hydroxylamine derivative are bonded with two acetylacetonato ligands in the Mn(III) mixed-ligand complexes.

Table 2. FTIR spectral data of the compounds [frequency (cm^{-1})]

$[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3]$	$[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2\text{L}^1]$	$[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2\text{L}^2]$	Band assignment ^a
430 m	417 m	425 m	$\nu(\text{Mn-O}), \delta(\text{Mn-O}=\text{C})$
460 m	482 m	487 m	$\nu(\text{Mn-O}), \nu(\text{C-CH}_3), \nu(\text{C}=\text{C})$

Table 2. continuation

550 m	613 m	575 m ^b	$\pi_{\text{ring}} + \nu(\text{Mn-O})$
588 s	654 s	633 m	$\nu(\text{Mn-O}),$ $\delta(\text{Mn-O=C}, \text{CH}_3\text{-C=O})$
669 ms	689 m	689 m	$\nu(\text{C-CH}_3), \nu(\text{Mn-O}),$ $\delta(\text{O=C-CH}_3)$
		771 m	$\gamma(\text{N-H}).$
778 s	782 s	778 w ^c	$\pi(\text{C-H})$
	875 m	876 m	$\delta(\text{COO})$
928 s	928 m	927 m	$\nu(\text{C-CH}_3)$
1020 s	1020 s	1023 s	$\gamma(\text{CH}_3)$
1185 w	1173 w	1180 w	$\delta(\text{C=CH})$
1253 s	1285 s	1281 m	$\nu(\text{C=C}), \nu(\text{C-CH}_3)$
		1312 m	$\nu(\text{C-N}), \delta(\text{N-H})$
	1338 s		$\nu_{\text{s}}(\text{COOH})$
1350 s		1361 s	$\delta(\text{CH}_3)$
1388 s	1388 w		$\delta(\text{CH}_3)$
	1458 m	1407 1462 m	$\nu_{\text{s}}(\text{COO})$ $\delta(\text{=CH})$
1512 s	1523 s	1514 s	$\nu(\text{C=C}), \delta(\text{C=CH})$
1567 s	1552 s	1551 s	$\nu(\text{C=C}), \delta(\text{C=CH})$
1595 s	1615 s	1595 s	$\nu_{\text{as}}(\text{COO})$
	1635 s		$\nu(\text{C=C})$
		1651 m	$\nu(\text{C=O})$
	1708 m		$\nu_{\text{as}}(\text{COOH})$
2920 w	2915 w	2920 w	$\nu(\text{C-H})$
	3229 m	3213 m	$\nu(\text{=CH})$
		3559 m	$\nu(\text{N-H})$
	3564 s	3400 s	$\nu(\text{O-H})$

^aRelative intensity; s-strong, m-medium, w-weak

^b π_{ring} , ring deformation out-of-plane that includes torsion τ O-C-C-C, τ O-C-C-H, τ CH₃-C-C-H

^c $\pi(\text{C-H}), \text{C-C-C-H}$ out-of-plane vibrations

Electronic absorption spectra

The spectral data and magnetic moments of the compounds are presented in Table III. In the complex Mn(III) acetylacetonate (13), there are two absorption bands, assigned to $\pi \rightarrow \pi^*$ transitions and one absorption band assigned to $\pi^* \rightarrow d$ transitions. These transitions have been also found in the spectra of the synthesized complexes, but they are shifted towards lower and higher frequencies, depending on the ligands structures.

Table 3. Electronic spectral data of the complexes recorded in ethanol
[frequency (cm⁻¹)/ ε_{max} (mol⁻¹ dm³ cm⁻¹)]

Complex	μ _{eff} /μ _B	ν (10 ⁴ cm ⁻¹) / ε				
		π → π*	π → π*	π* → d	d → d*	d → d*
[Mn(C ₅ H ₇ O ₂) ₃]	4.90	40.8/17500	36.4/24000	30.7/9500	24.8/950	17.5/100
[Mn(C ₅ H ₇ O ₂) ₂ L ¹]	4.76	41.6/31000	35.2/12000	30.2/17500	24.3/1000	17.6/70
[Mn(C ₅ H ₇ O ₂) ₂ L ²]	4.81	42.0/22500	35.9/14500	30.3/11000	24.8/1500	17.5/170

In the VIS electronic absorption spectrum there are two absorption bands assigned to d→d* transitions in the complexes (I, II).

This band could be assigned to a charge transfer transition, or even to d→d* transition. The colour of the complexes is probably due to these transitions.

The colour of transition metal complexes is originated from d-orbitals. It is known that ligand splits d-orbitals of central ion in two groups. This splitting is weak and the excitation of electron from t_{2g} to e_g orbitals is always observed in visible electronic absorption spectra.

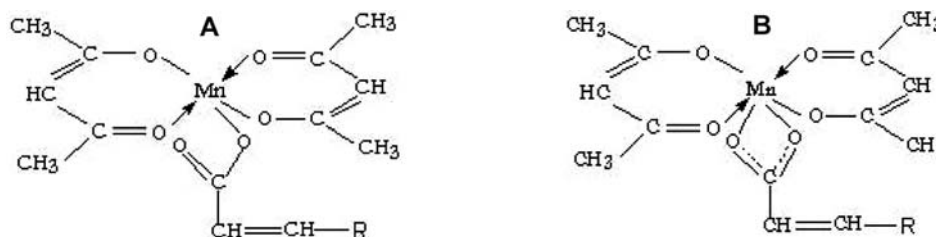
Magnetic properties

An indication of the most probable stereochemistry of the synthesized Mn(III) complexes is given by its colour and magnetic moment. Namely, black manganese(III) acetylacetonate complex usually have an octahedral configuration.

The room temperature effective magnetic moments of the manganese(III) complexes with mixed ligands are in the range of 4.76-4.9 μ_B, which corresponds to four unpaired electrons typical of the d⁴ system.

It is supposed that in mixed-ligand complexes the ligand has localized π-bond and do not favour electron-pairing. The Jahn-Teller effect due to an unequal filling up of t_{2g} and e_g orbitals yields a distorted octahedral geometry in complex. These complexes have a dark green to green colour.

The proposed structures of the complexes shown in Fig 3 are consistent with the related data (5).



R = -COOH (Compound I), R = -CONHOH(Compound II),

Fig. 3. Proposed structure of the complexes with mixed ligand

CONCLUSIONS

The ligands of maleic acid (L^1) and its hydroxylamin derivative (L^2), formed with Mn(III) acetylacetonato complex the mixed-ligand complexes of the general formula $[Mn(C_5H_7O_2)_2L]$. The complexes were synthesized and characterized by elemental analysis, magnetic susceptibility measurements, IR and UV/VIS spectra. Replacement of the acetylacetonate ligand by the corresponding acid ligand has been confirmed in Mn(III) acetylacetonate. Based on the obtained experimental data and literature indications, the structural formulae to these compounds were assigned.

REFERENCES

1. Blank, W.J., Z.A. He and E.T. Hessel: Catalysis of the isocyanate-hydroxyl reaction by non-tin catalysts. *Progress in Organic Coatings* **35** (1999) 19-29.
2. Seneker, S.D. and T.A. Potter: Solvent and Catalyst Effects in the Reaction of Aliphatic Isocyanates with Alcohols, Water-Borne and Higher Solids Coatings, Symposium, New Orleans, Feb., 1989, p. 369-376
3. Kresta, E., C. Shen and S.Lin: Steric and Solvation Effects in Catalysis of Urethanes. *Soc. Plast. Eng., Tech. Pap.* **25** (1979) 435-438.
4. L.B. Weisfeld: The Estimation of Catalytic Parameters of Metal Acetylacetonates in Isocyanate Polymerization Reactions. *Journal of Applied Polymer Science* **5** (1961) 424-427.
5. Nikolaev, A.F., K.V. Belogorodskaya, V.G. Shibalovich and E.D. Andreeva: Poluchenie i svoistva bisacetilacetatokarboksilatov marganca III. *Zh.P.H* **12** (1973) 2718-2725.
6. Shibalovich, V.G., K.V. Belogorodskaya and V.G. Karkozov: Novye kataliticheskie sistemy na osnove khelatnih kompleksov marganca(III) i ikh primenenie v processakh polimerizacii i otverzheniya. *Plast. massy* **11** (1989) 18-25.
7. Stamenković, J., S. Cakić and G. Nikolić: Studija katalitičke selektivnosti vodenih dvokomponentnih poliuretanskih sistema FTIR spektroskopijom. *Hemijska industrija* **57** (2003) 559-562.
8. Stamenković, J., S. Cakić, S. Konstantinović and S. Stoilković: Catalysis of the isocyanate hydroxyl reaction by non-tin catalysts water borne two component polyurethane coatings. *Facta Univerzitatatis, Series Working and Living Environmental Protection* **2** (2003) 235-242.
9. Cakić, S., J. Stamenković and G. Nikolić: Ispitivanje procesa umrežavanja vodenih dvokomponentnih poliuretanskih premaza korišćenjem selektivnijih nekalajnih katalizatora. *Svet polimera* **7,1** (2004)1-6.
10. Diaz-Acosta, J., J.F. Baker and P. Pulay: Calculated and experimental geometries and infrared spectra of metal tris-acetylacetonates: vibrational spectroscopy as a probe of molecular structure for ionic complexes. Part II, *Spectrochimica Acta Part A* **59** (2003) 363-377.
11. Silverstein, R.M., G.C. Bassler and T.C. Morrill: *Spectrometric identification of compounds*, Wiley, New York (1974) 254.
12. K. Nakamoto: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1986) 302.

**ФИЗИЧКО-ХЕМИЈСКА КАРАКТЕРИЗАЦИЈА Mn(III)
КОМПЛЕКСА СА МЕШОВИТИМ ЛИГАНДИМА НА БАЗИ
АЦЕТИЛАЦЕТОНАТА И МАЛЕИНСКЕ КИСЕЛИНЕ
И ЊЕНОГ ХИДРОКСИЛАМИНСКОГ ДЕРИВАТА**

*Сузана М. Цакић, Горан С. Николић,
Јаков В. Стаменковић и Сандра С. Константиновић*

Синтетисна су два нова Mn(III) мешовито-лигандна комплекса са два ацетил-ацетонатна лиганда и једним малеинским лигандом као и његовим хидроксиламинским дериватом. Изоловани комплекси су окарактерисани елементарном анализом, FTIR и UV/VIS спектроскопским методама, као и магнетним мерењима. Утврђено је да је у комплексу Mn(III) ацетилацетонату дошло до замене ацетилацетонатног лиганда одговарајућим киселинским лигандом. На основу добијених резултата и литературних података овим једињењима су приписане одговарајуће структурне формуле.

Received 21 March 2005
Accepted 6 September 2005