

New Optically Active Manganese(II) Complexes with Schiff Bases Obtained from (1R,2R)-(-)-1,2-Cyclohexanediamine and Salicylaldehyde Derivatives

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Manganese ions were found in oxygen evolving complex (OEC) in the photosystem II (PS II), which harvests the light energy to split H₂O into O₂, protons and electrons [1,2]. OEC structure details are not known yet, thus, manganese complexes are used as models of this biological system [3,4]. Besides that manganese coordination compounds with optically active Schiff bases were reported as catalysts of oxidation reactions, especially in enantioselective epoxidation of olefins [5–10]. We present manganese(II) complexes with chiral Schiff bases derived from (1R,2R)-(-)-1,2-cyclohexanediamine [(–)chxn] and salicylaldehyde (sal), 2-hydroxy-1-naphthylaldehyde (naft) or 2-hydroxy-5-nitrobenzaldehyde (nsal). Ligands were prepared by condensation of diamine and appropriate aldehyde (1:2 molar ratio) in methanol solution according to [11]. Complexes were obtained in reaction of Mn(CH₃COO)₂·4H₂O (0.02 mol) and Schiff base (0.02 mol, hot ethanol, argon atmosphere). Obtained dark yellow or brown precipitates were isolated and dried in vacuum. The results of elemental analyses confirmed the compositions proposed for Mn(–)chxn(sal)₂·2H₂O (**1**); Mn(–)chxn(naft)₂·2C₂H₅OH (**2**); Mn(–)chxn(nsalsal)₂·C₂H₅OH·H₂O (**3**). In order to confirm the presence of water and ethanol molecules, thermal analysis in nitrogen was performed and the results are listed in Table 1.

Table 1. Results of thermal analysis.

Compound	Heat effect	Temperature (°C)			Weight loss on TG (%)		Detached molecules
		T _i	T _m	T _f	Found	Calc.	
1	endo	195	215	230	4.0	4.4	H ₂ O
	endo	245	330	405	15.0	–	
	endo	405	445	570	22.0	–	
2	endo	115	160	175	7.5	8.1	C ₂ H ₅ OH C ₂ H ₅ OH
	endo	195	215	235	8.0	8.1	
	–	275	310	460	–	–	
	endo	370	400	425	12.0	–	
3	endo	105	145	195	9.0	8.7	C ₂ H ₅ OH
	exo	285	320	350	11.0	–	

T_i – initial temperature; T_m – maximum temperature; T_f – final temperature.

Thermal analysis of **(1)** revealed an endothermic process with maximum at 215°C, and a mass loss, which can be assigned to the detachment of one water molecule. The second one is evolved, most probably, in the next endothermic stage (maximum at 330°C), which is also connected with a mass loss. However, this effect is complicated by the simultaneous Schiff base decomposition reaction (onset at 245°C). Analysis of thermoanalytical curves suggests the dissociation of two ethanol molecules in the first of two endothermic stages for **(2)** (Table 1), whereas for **(3)** only one endotherm stage, associated with ethanol molecule detachment, was detected. The observed maximum temperatures of endotherms are much higher than the water and ethanol boiling points, due to coordination of these molecules.

IR spectra of **(1)**, **(2)** and **(3)** revealed $\nu_{\text{C=N}}$ absorption bands shifted towards lower frequencies (*ca.* 10–15 cm^{-1}) in comparison to free ligands (1620–1640 cm^{-1}), what can be assumed as a result of imine nitrogens metallation [12]. Also the phenolic $\nu_{\text{C-O}}$ band (1270–1300 cm^{-1}) is shifted (10–40 cm^{-1}) towards higher energies after complexation [13]. From group theory calculations, for the coordination sphere micro-symmetry (C_{2v}), two Mn–N and two Mn–O stretching vibrations bands can be expected [14]. Absorption bands observed at 490 and 445 cm^{-1} in the spectrum of **(3)** as well as at 508 and 466 cm^{-1} for **(2)** can be assigned to Mn–O vibrations, what is consistent with the literature data for similar complexes [15]. Mn–N vibrations bands were observed at 383 and 359 cm^{-1} for **(3)** and at 352 and 312 cm^{-1} for **(2)**. In the case of **(1)** the Mn–O bands probably coincide with the ligand vibration bands and only one broad Mn–N band at 354 cm^{-1} is noticeable. Strong O–H band in the 3420–3390 cm^{-1} range, observed in the spectra of complexes, confirmed the presence of ethanol and/or water molecules.

Coordination of ligands has also an evidence in LSIMS. Peaks corresponding to $[\text{MnL}]^+$ fragments were detected in the spectra of **(1)**, **(2)** and **(3)** at 375, 475 and 465 *m/z* respectively. Furthermore, the spectrum of **(1)** exhibits peak from $[\text{Mn}_2\text{L}_2]^+$ (*m/z* – 750). This dimeric fragment has been found also in the spectra of structurally similar μ -phenoxy dimers and it can be related to dimeric species in the compound studied (Fig. 1) [16].

Electrochemical measurements were carried out in order to check a possible catalytic activity of the complexes studied. Measurements were performed at the following conditions: room temperature, 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte, acetonitrile solution, argon atmosphere, platinum button as the working electrode, platinum wire as the counter electrode and a silver wire as the reference electrode, using an AutoLab (EcoChemie) instrument. Cyclic voltammograms for all complexes exhibit the single couple Mn(II)/Mn(III) in the potential range –0.24–0 V (*vs.* Ag/Ag⁺). Peak parameters for the scan rate 50 mV/s are listed in Table 2. Relation between the peak current intensity and the square root of the scan rate is linear, indicating reversible or quasireversible electron transfer. Additional evidence of fast charge transfer is anodic to cathodic current ratio, which is near to unity. The oxidation potential for **(3)** was +40 mV, while for **(1)** and **(2)**: –165 mV and –85

mV respectively. Higher stability of Mn(II) in (3) can be related to the strong σ -acceptor properties of nitro group at C-5 position in phenyl ring.

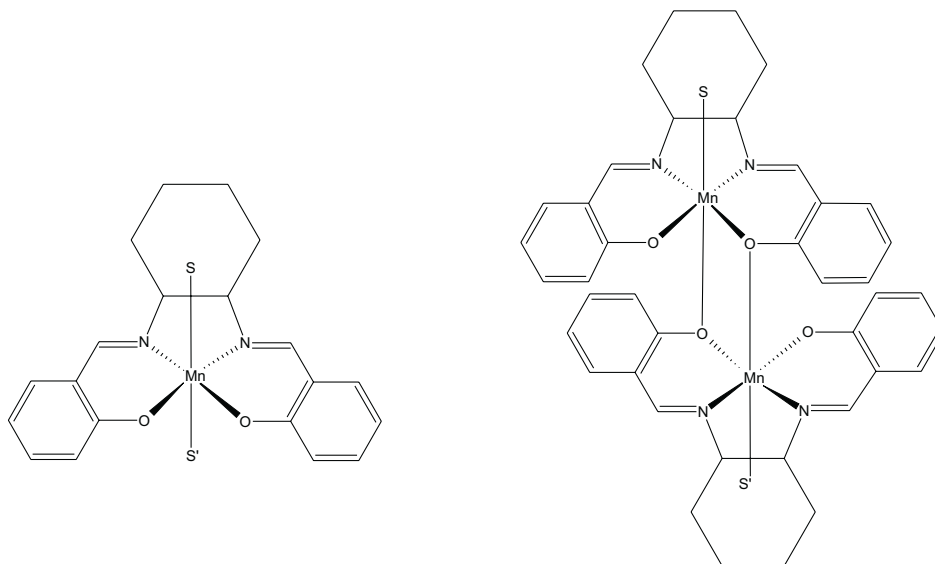


Figure 1. Possible structures of manganese surroundings (S, S' – solvent molecules).

Table 2. Electrochemical data.

Compound	$E_{1/2}/V$	E_{ox}/V	E_{red}/V	$\Delta E/mV$	I_{ox}/I_{red}
1	-0.226	-0.165	-0.287	122	0.972
2	-0.162	-0.085	-0.239	154	0.991
3	0.004	0.040	-0.048	88	0.979

Presented results are in favour of the distorted octahedral geometry of manganese(II) with Schiff base occupying four equatorial basal sites, while water or ethanol molecules occupying the axial positions. Dimeric form observed in mass spectrum of (1) can be present in the solid state, but the monomeric one prevailed. Results of electrochemical data suggest a catalytic activity of the complexes (especially 3). Further research on the influence of the ligand electronic and steric effects on the complex geometry will be reported.

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