



Synthesis and Structural Characterization of Supramolecular Mn(II)-Li(I) Complex with Salen-Type Bisoxime

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Supramolecular manganese(II)-Li(I) complex, $[\text{MnL}(\text{OH})(\text{H}_2\text{O})\text{Li}]_n$, has been prepared and characterized by elemental analyses, FT-IR, UV-visible spectra, molar conductance measurement and X-ray crystallography (where $\text{H}_2\text{L} = 4,4',6,6'$ -tetrachloro-2,2'-[ethylenedioxybis(nitrilomethylidene)]diphenol). The complex is self-assembled using various non-covalent interactions including hydrogen bonding interactions and π - π stacking to form chain supramolecular structure.

Key Words: Salen-type bisoxime, Complex, Synthesis, Crystal structure.

INTRODUCTION

In the past decades, the complexes containing transition metal ions and various Schiff-base ligands have been extensively investigated due to their novel structures and potential applications in many fields¹. Particularly, a large number of transition metal complexes of Salen-type ligands derived from the condensation of salicylaldehyde and its derivatives with various primary amines become the hot topics of contemporary research². The Salen-type bisoxime ligands have been reported by using an O-alkyloxime unit (-CH=N-O-(CH)₂-O-N=CH-) instead of the (-CH=N-(CH)₂-N=CH-) group, which can lead to different and novel properties and structures of the resulted complexes³⁻⁵. but the Mn(II) complexes with salen-type bisoxime ligands have been reported rarely. In this paper, we report the synthesis, characterization and X-ray crystal structure of the μ -oxo bridged $[\text{MnL}^2(\text{OH})(\text{H}_2\text{O})\text{Li}]_n$ complex with tetradentate Salen-type bisoxime ligand. The complex is self-assembled using various non-covalent interactions including hydrogen bonding interaction⁶ and π - π stacking⁷ to form chain supramolecular structure.

EXPERIMENTAL

3,5-Dichlorosalicylaldehyde was purchased from Alfa Aesar and used without further purification. 1,2-Bis(aminoxy)ethane was synthesized according to an analogous method reported earlier^{8,9}. The other reagents and solvents were of analytical reagent grade and were used without further purification. C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analyses for Mn and Li were detected by an IRIS

ER/S-WP-1 ICP atomic emission spectrometer. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (4000-500 cm^{-1}) and CsI (500-100 cm^{-1}) pellets. ¹H NMR spectra were determined by German Bruker AVANCE DRX-400 spectroscopy. X-Ray single crystal structure determination was carried out on a Bruker Smart 1000 CCD diffractometer. Molar conductance value measurement was carried out on a model DDS-11D type conductivity bridge using $1.0 \times 10^{-3} \text{ mol} \times \text{dm}^{-3}$ solution in DMF at 18 °C. Melting points were obtained by use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected.

General procedure

4,4',6,6'-Tetrachloro-2,2'-[ethylenedioxybis(nitrilomethylidene)]diphenol (H_2L): H_2L was prepared according to an analogous method reported earlier^{5,10,11}. By mixing of 3,5-dichloro-2-hydroxybenzaldehyde (399.0 mg, 2.10 mmol) and 1,2-bis(aminoxy)ethane (180.1 mg, 1.05 mmol) in ethanol solution (8 mL), a pale-yellow solution was obtained. After the solution had been stirred at 55 °C for 3 h, the mixture was filtered, washed successively with ethanol and hexane, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to yield 318.95 mg of colourless crystalline solid. Yield 72.8 %. m.p. 204-205 °C. Anal. calcd. (%) for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4\text{Cl}_4$: C, 43.87; H, 2.76; N, 6.39. Found (%): C, 43.95; H, 2.68; N, 6.28. ¹H NMR (400 MHz, DMSO-*d*₆, δ , ppm) 4.48 (s, 4H, CH₂), 7.53 (t, $J = 2.6$ Hz, 2H, Ar-H), 7.61 (t, $J = 2.6$ Hz, 2H, Ar-H), 8.47 (d, $J = 2.0$ Hz, 2H, =C-H), 10.38 (s, 2H, OH).

[MnL(OH)(H₂O)Li]_n: A solution of Mn(II) acetate tetrahydrate (12.3 mg, 0.05 mmol) in methanol (15 mL) was added dropwise to a solution of H₂L (21.9 mg, 0.05 mmol) in THF (45 mL) at room temperature. The colour of the mixing solution turned to yellow immediately. After 10 min, LiCl (4.2 mg, 0.1 mmol) dissolved in the minimum amount of water, was poured into the solution. After continuing stirring for 5 days at room temperature, the mixture was filtered and the filtrate was allowed to stand at room temperature for several weeks. Then the solvent partially evaporated and yellow needle-like single crystals suitable for X-ray crystallographic analysis were obtained. Yield: 35.7 %. Anal. calcd. (%) for C₁₆H₁₃Cl₄LiMnN₂O₆ ([MnL(OH)(H₂O)Li]_n): C, 36.12; H, 2.39; Li, 1.30; Mn, 10.33; N, 5.22. Found (%): C, 36.11; H, 2.43; Li, 1.31; Mn, 10.29; N, 5.24.

X-Ray structure determination: The crystal data and structure refinement for [MnL(OH)(H₂O)Li]_n is given in Table-1. The single crystal of [MnL(OH)(H₂O)Li]_n with approximate dimension of 0.40 mm × 0.13 mm × 0.02 mm were placed on a Bruker Smart 1000 CCD area detector. The diffraction were collected using a graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXL-97 and Fourier difference technique and refined by full-matrix least-square method on F². All hydrogen atoms were added theoretically.

TABLE-1 CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPLEX	
Empirical formula	C ₁₆ H ₁₃ Cl ₄ LiMnN ₂ O ₆
Formula weight	532.96
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Cell dimensions	a = 17.2609(18) Å, b = 15.1325(16) Å, c = 7.7642(9) Å, β = 97.1480(10)
Volume	2012.3(4) Å ³
Z	4
Density (calculated)	1.759 mg/m ³
Absorption coefficient	1.225 mm ⁻¹
F ₍₀₀₀₎	1068
Index ranges	-20 ≤ h ≤ 19, -14 ≤ k ≤ 18, -9 ≤ l ≤ 9
Reflections collected/unique	5052/1762 [R _(int) = 0.0314]
Independent reflections	2092
Data/restraints/parameters	1762/0/137
Goodness of fit indicator	0.981
R [I > 2σ(I)]	R ₁ = 0.0441, wR ₂ = 0.1153
Largest diff. peak and hole	0.694 and -0.367 e. Å

RESULTS AND DISCUSSION

Crystal structure of [MnL(OH)(H₂O)Li]_n: Interaction of Mn(II) acetate tetrahydrate with the appropriate Salen-type ligand in a basic medium yields [MnL(OH)(H₂O)Li]_n depending on the time of reaction. Suitable single crystals of the complex was obtained by natural evaporation method. X-Ray single crystal determination shows that the complex forms a self-assembling continual supramolecular structure by hydrogen bonding interactions and π-π stacking. The atom numbering and the chain supramolecular structure of the complex is given

in Fig. 1. Selected bond distances and angles of the complex are listed in Table-2.

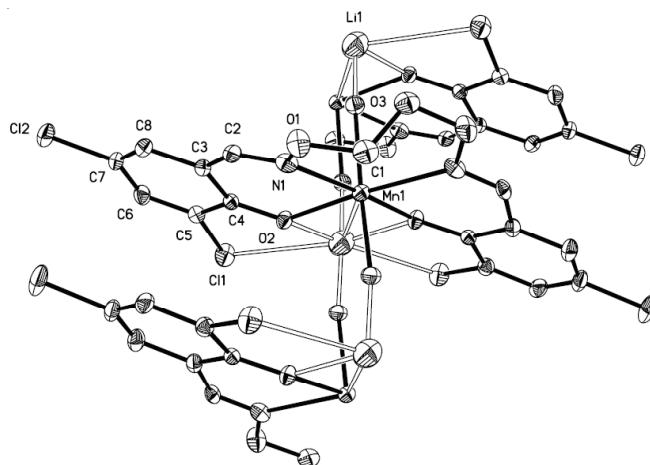


Fig. 1. Molecule structure of the title complex with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

The complex has been synthesized from the reaction of the ligand (H₂L), Mn(II) acetate tetrahydrate and LiCl in mixing solution and revealed by X-ray crystallography. The complex is crystallized in the monoclinic system, space group C2/c. The structural of [MnL²(OH)(H₂O)Li]_n adopts a slightly distorted octahedral geometry with a hexa-coordinated Mn(II) center. L²⁻ unit behaves as a tetradentate agent *via* two phenolic oxygen and two oxime nitrogen atoms, which are in the equatorial positions. The Mn-O (phenolic) bond of 2.122(2) Å and Mn-N(oxime) bond of 2.307(3) Å are in agreement with the average bond lengths seen for the corresponding bonds in the Mn(II) complexes bearing tetradentate salen-type ligands in a planar fashion¹². The four N₂O₂ donor atoms of L²⁻ unit are approximately coplanar and the dihedral angle of O2-Mn1-N1 and O2⁻-Mn1-N1ⁱ is 2.08°. The axial sites of Mn(II) atom is occupied by two oxygen atoms of one coordinated water molecule and one hydroxy group in a considerably large angle of O3-Mn1-O3ⁱ (167.63(14)°). It is noticeably that the bond distance Mn1-O3 (2.152(3) Å) is the same with Mn1-O3ⁱ, which indicate the same coordination abilities of the two μ-oxo bridges.

In addition, every monomer of the complex contains a Li(I) atom. The coordination geometry around the Li(I) (Li1) atom can be best described as slightly distorted square pyramidal geometry with unexpected penta-coordinated. Two phenolic oxygen atoms (O2ⁱⁱ and O2^{iv}) and two chlorine (Cl1ⁱⁱ and Cl1^{iv}) atoms of L²⁻ unit constitute the basal plane and one oxygen atoms from the bridging hydroxy group in the axial position. The distance of Mn1...Li1ⁱⁱ (2.800(15) Å) is significantly longer than all the Mn-O and Mn-N bonds in the complex, indicating a weaker intermetal interaction. The complex has four intermolecular hydrogen bonds (O3-H3A...O2, O3-H3B...O2, O3-H3A...Cl1 and O3-H3B...Cl1) which help to connect the individual monomer to form and stabilize the three-dimensional structure (Table-3). The special interest of the complex is its self-assembling Mn(II)-O-Li(I) chain array stacked by hydrogen bonding interactions and π-π stacking of

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR THE TITLE COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Mn1-O2	2.122(2)	Mn1-N1 ⁱ	2.307(3)	Li1-O2 ^{iv}	2.058(10)
Mn1-O2 ⁱ	2.122(2)	Mn1-N1	2.307(3)	Li1-O2 ⁱⁱ	2.058(10)
Mn1-O3 ⁱ	2.152(3)	Mn1-Li1 ⁱⁱ	2.800(15)	Li1-C11 ^{iv}	3.003(7)
Mn1-O3	2.152(3)	Li1-O3 ⁱⁱⁱ	1.761(3)	Li1-C11 ⁱⁱ	3.003(7)
Bond	Angles	Bond	Angles	Bond	Angles
C(10)-N(1)-O(1)	113.3(5)	C(11)-C(12)-C(13)	116.9(6)	O(4)-C(23)-C(24)	121.9(6)
O2-Mn1-O2 ⁱ	93.96(13)	N1 ⁱ -Mn1-N1	106.84(16)	O3-Mn1-Li1 ⁱⁱ	96.18(7)
O2-Mn1-O3	94.07(10)	O2-Mn1-Li1 ⁱⁱ	46.98(6)	Li1-O3-Mn1	165.4(5)
O3 ⁱ -Mn1-O3	167.63(14)	N1-Mn1-Li1 ⁱⁱ	126.58(8)	O2 ⁱⁱ -Li1-C11 ⁱⁱ	68.11(9)
O2-Mn1-N1	79.61(10)	O3-Mn1-N1	84.78(11)	C11 ^{iv} -Li1-C11 ⁱⁱ	126.4(5)

Symmetry transformations used to generate equivalent atoms: (i) $-x+1, y, -z+1/2$ (ii) $-x+1, -y+1, -z$ (iii) $-x+1, y, -z-1/2$ (iv) $x, -y+1, z-1/2$.

TABLE-3
HYDROGEN BONDS [Å, °] FOR THE TITLE COMPLEX

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠DHA	Symmetry
O3-H3A...O2	0.85	2.18	2.913(3)	144	$-x+1, -y+1, -z$
O3-H3A...C11	0.85	2.79	3.393(3)	129	$-x+1, -y+1, -z$
O3-H3B...O2	0.85	1.93	2.714(3)	153	$x, -y+1, z-1/2$
O3-H3B...C11	0.85	2.89	3.398(3)	120	$x, -y+1, z-1/2$

neighboring benzene rings (Fig. 2). Two neighboring monomers have the anti-conformation, the angle of the two neighboring benzene rings is $0.87(3)^\circ$ and the mean distance between the two neighboring benzene rings is 3.638 \AA , indicating weak π - π stacking interaction.

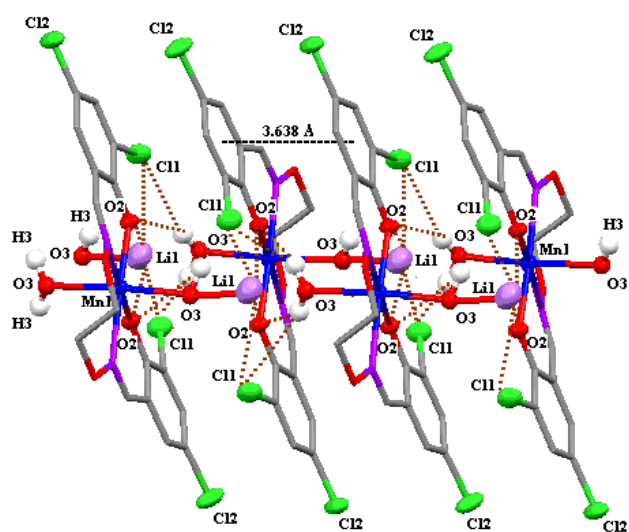


Fig. 2. View of the 1D chain supramolecular structure of Mn(II)-Li complex along the a axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

Molar conductance: Molar conductance values of the complex at 18°C of $10^{-3} \text{ mol} \times \text{dm}^{-3}$ DMF solution is $7.6 \text{ S} \times \text{cm}^2 \times \text{mol}^{-1}$, indicating that the complex is non-electrolyte. This implies that all the Mn(II) and Li(I) atoms in the complex are firmly held in the coordination sphere in solution.

IR spectra: The main characteristic infrared spectral bands of the free ligand and its Mn(II)-Li(II) complex are shown in Table-4. IR spectrum of H_2L exhibits characteristic $\text{C}=\text{N}_{\text{oxime}}$ stretching band at 1609 cm^{-1} , while the $\text{C}=\text{N}_{\text{oxime}}$ of the complex was observed at 1603 cm^{-1} . The $\text{C}=\text{N}_{\text{oxime}}$ band is shifted

TABLE-4
KEY IR BANDS FOR THE LIGAND AND THE TITLE COMPLEX (cm^{-1})

Compound	$\nu(\text{O-H})$	$\nu(\text{CH}_{\text{arom}})$	$\nu(\text{CH}_2)$	$\nu(\text{C}=\text{N})$	$\nu(\text{C-O})$
H_2L	3427	3078	2963, 2899	1609	1277
Complex	3414	3079	2955, 2891	1603	1304

to lower frequency by *ca.* 6 cm^{-1} upon complexation. At the same time, $\text{C-O}_{\text{phenol}}$ stretching frequency appears as a strong band in the compound. This band occurs at 1277 cm^{-1} for H_2L and at 1304 cm^{-1} for the complex. The $\text{C-O}_{\text{phenol}}$ stretching band is shifted to higher frequency by 27 cm^{-1} upon complexation. These data suggest the coordination of the ligand in their dianionic form to the Mn(II) atom through the phenol oxygen and the oxime nitrogen atoms and show the tetradentate character of the ligand in the complex¹³⁻¹⁵. Additionally, strong and broad bands at 3414 cm^{-1} indicates that O-H is existent in the complex.

The far-infrared spectrum of the complex is also obtained in the region $500\text{-}100 \text{ cm}^{-1}$ in order to identify frequencies due to the $\nu(\text{Mn-O})$ and $\nu(\text{Mn-N})$ bonds. IR spectrum of the complex shows $\nu(\text{Mn-N})$ and $\nu(\text{Mn-O})$ vibrational absorption frequencies at 473 and 448 cm^{-1} , respectively, which are consistent with the literature frequency values¹⁶. These bands are observed as new peaks for the complex are not present in the spectrum of the free ligand.

UV-visible absorption spectra: The UV-visible absorption spectra of the ligand H_2L and its corresponding complex in diluted DMF solution are shown in Fig. 3. It can be seen that the absorption peaks of the complex are obviously different from those of the free ligand upon complexation. Compared with the complex, an important feature of the absorption spectrum of H_2L is shown that one absorption peak is observed at 324 nm , which is absent in the spectrum of the complex. The other feature is that the absorption peak at 268 nm in H_2L is shifted to 266 nm in the complex and a new absorption peak at 377 nm was observed in the complex, indicating that the coordination of Mn(II) atom with H_2L .

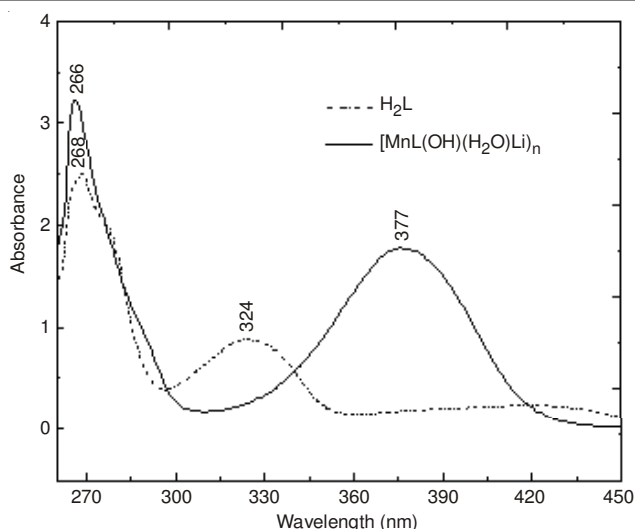


Fig. 3. UV-visible absorption spectra of H_2L (---) and the title complex (—) in DMF (1.0×10^{-4} mol/L)

Conclusion

According to the data and discussion above, the new complex, $[MnL(OH)(H_2O)Li]_n$, has been synthesized and structurally characterized. In FT-IR spectra of the complex, the $\nu(M-O)$ and $\nu(M-N)$ vibrational absorption frequencies have been observed. The structure of the complex has been determined by X-ray diffraction technique, The complex forms a one-dimensional infinite self-assembling chain supramolecular structure by hydrogen bonding interactions and $\pi-\pi$ stacking of neighbouring benzene rings.

Supplement data: Further details of the crystal structure investigation(s) may be obtained from the Cambridge Crystallographic Data Centre, Postal Address: CCDC, 12 Union Road, CAMBRIDGE CB2 1EZ, UK. Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail:

deposit@ccdc.cam.ac.uk, on quoting the depository number CCDC 712160.

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