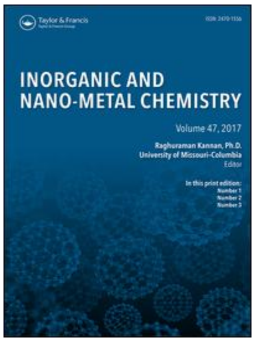

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Muhammet Kose

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Two seven-coordinate Mn(II) complexes derived from pentadentate ligands: Structural characterization and investigation of photophysical properties

Muhammet Kose

Chemistry Department, Kahramanmaras Sutcu Imam University, Kahramanmaras, 46050, Turkey.

Corresponding author Tel.: +90 344 280 1408; fax: +90 344 280 1352. E-mail address: muhammetkose@ksu.edu.tr (Muhammet Kose)

Abstract

Two mononuclear Mn(II) complexes derived from pentadentate ligands were prepared and characterized. Molecular structures of the complexes were determined by X-ray diffraction studies. Mn(II) ions in both structures are seven-coordinate with approximate pentagonal bipyramidal geometry where the pyridine-diimine unit and phenolic or alcoholic oxygen atoms (N_3O_2) of the ligand are located at the pentagonal plane and two exogenous ligands at the axial positions. In the structure of $[Mn(HL_2)Cl(CH_3OH)]\cdot 2(CH_3OH)$, methanol solvates link complex molecules into a 1D hydrogen bonded chain. Emission spectra of the complexes shows only one emission band in the 595-625 nm range upon excitation in 585-615 nm range.

Keywords

Seven-Coordinate Mn(II); Pentadentate ligand; Molecular structure; Emission spectra

1. Introduction

Nitrogen–oxygen donor pentadentate ligands and their metal complexes have received considerable attention owing to their applications in several areas including catalysis, transport processes and mimicking of several biological compounds [**1–5**]. Many ligand nitrogen– oxygen donor systems have been studied to mimic the function of natural carriers in recognizing and transporting specific molecules or ions and for understanding and reproducing the catalytic activity of metallo-enzymes [**6**]. Pentadentate (N_3O_2 or N_5 type) Schiff base ligands derived from 2,6-diacetylpyridine and 2,6-diformylpyridine are of interest to prepare macrocyclic and acyclic Schiff base metal complexes [**7–11**]. These ligands often bind to the metal ions with all five donor atoms resulting in six or seven-coordinate complexes (with one or two auxiliary ligands) depending on the metal ions. The Mn(II) ion, for example, generally forms seven-coordinate complexes with these pentadentate Schiff base ligands [**12–16**]. Pentadentate Schiff base ligands derived from 2,6-diacetylpyridine and 2,6-diformylpyridine provide pentagonal coordination site to obtain seven-coordinate Mn(II) complexes with two auxiliary anions [**16**]. The factor leading to seven-coordinate structure is that the rigid pyridine-diimine section in these ligands constrains three nitrogen donors to be planar and to occupy two bite angles of 136.41(15)°, leaving enough space for two further donors in the same plane resulting in a pentagonal plane [**16**].

Recently, we reported mono-, di- and tri-nuclear seven-coordinate Mn(II) complexes derived from 2,6-diformylpyridine and 2-aminophenol [**17**]. In continuation of our interest in seven-coordinate Mn(II), here we report the synthesis, structural characterization, thermal and photophysical properties of two Mn(II) complexes.

2. Experimental

2.1 General methods

All starting materials and organic solvents were purchased from Sigma-Aldrich and used as received, unless noted otherwise. 2,6-Diformylpyridine was prepared by oxidation of 2,6-pyridinedimethanol using manganese dioxide according to the literature method [**18**] and used without further purification. IR spectra were performed on a Perkin Elmer Paragon 1000 PC. CHN analyses were performed using a CE-440 Elemental analyser. The ^{1}H NMR spectra were performed on a Bruker Avance 500. The electronic spectra in the 200–900 nm range were obtained on a Shimadzu UV-1800 UV-Vis spectrophotometer. The single-photon fluorescence spectra were collected on a Perkin Elmer LS55 luminescence spectrometer. The thermal analyses of the complexes were performed on a Perkin Elmer Pyris Diamond.

2.2 X-ray structures solution and refinement for the complexes

Data collection and cell refinement for X-ray crystallography were completed using a Bruker APEX2 CCD diffractometer and data reduction was performed using Bruker SAINT. Diffraction data were measured at 150(2) K using Mo-*K*□ radiation with a Bruker ApexII diffractometer [**19**]. SHELX-2014 was used to solve and refine the structures [**19**]. SADABS-2009/1 was used for absorption correction [**20**]. The structure was solved by direct methods and refined on F^2 using all reflections using the SHELXTL software [**21**]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters. Hydrogen atoms bonded to carbon atoms and hydrogen atoms bonded to O4 and O5 atoms in [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH) were inserted at calculated positions using a riding model.

Rest of the H atoms bonded to oxygen atoms in both complexes were located from difference maps and refined freely. In $[Mn(HL1)(Cl)(CH_3OH)]\cdot 2(CH_3OH)$, in each complex molecule, one of the phenolic OH groups is deprotonated and the hydrogen atom bonded to the phenolic oxygen atom is disordered over two phenolic oxygen atoms (O1 and O2) and their occupancies were fixed with 0.5-0.5. Details of the crystal data and refinement are given in **Table 1**.

2.3 Synthesis of the Schiff base ligands (H_2L1 and H_2L2)

The ligands were synthesised by the reaction of 2,6-diformylpyridine (0.135 g, 1 mmol) and 2-amino-*p*-cresol (0.246 g, 2 mmol) or 2-aminobenzylalcohol (0.246 g, 2 mmol) in refluxing methanol. After four hours reflux, the solvent was removed on a rotary evaporator. The ligand H_2L1 was obtained as yellow powder while H_2L2 as yellowish oil. The ligands were characterized by ^1H NMR, IR spectra and micro (CHN) analysis.

$H_2L1\cdot 1/2H_2O$: Yellow powder, yield: 0.301 g (85%). Elemental analyses for $C_{21}H_{19}N_3O_2\cdot 1/2H_2O$ (354.4 g/mol): Calcld.: C, 71.17; H, 5.69; N, 11.86. Found: C,70.85; H,5.45; N,11.60%. IR (KBr, cm^{-1}): 3405, 2945, 1620, 1572, 1492, 1351, 1245, 1182, 1087, 1032, 984, 960 cm^{-1}. NMR: ^1H ($CDCl_3$ as solvent, δ ppm) 10.15 (*br*, PhOH), 8.72 (*s*, 2H, -N=CH), 8.18 (*d*, 2H pyridine), 7.83 (*t*, 1H pyridine), 7.11(*s*, 2H, aromatic), 6.95 (*d*, 2H, aromatic), 6.89 (*d*, 2H, aromatic), 2.21 (*s*, 6H, C-CH_3), 1.62 (*br*, H_2O).

H_2L2: Yellowish oil, yield: 0.322 g (93%). Elemental analyses for $C_{21}H_{19}N_3O_2$ (345.4 g/mol): Calcld.: C, 73.03; H, 5.54; N, 12.17. Found: C,72.86; H,5.39; N,11.83%. IR (ATR, cm^{-1}): 3415, 2945, 2920, 1624, 1577, 1495, 1353, 1175, 1081, 1035, 974, 955 cm^{-1}. NMR: ^1H ($CDCl_3$ as solvent, δ ppm) 8.75 (*s*, 2H, -N=CH), 8.17(*d*, 2H pyridine), 7.88 (*t*, 1H pyridine), 7.09-7.28 (*m*, 8H aromatic), 4.61 (*s*, 4H, C-CH_2-OH).

2.4 Synthesis of $[Mn(HL1)(Cl)(CH_3OH)]\cdot 2(CH_3OH)$

To a refluxing solution of the ligand $H_2L1\cdot 1/2H_2O$ (0.354 g, 1 mmol) in methanol (30 mL), $MnCl_2.4H_2O$ (0.197 g, 1 mmol) was added resulting in a red clear solution. The reaction solution was further refluxed for 4 hours. Upon cooling to the room temperature, a red precipitate formed was filtered and washed with cold MeOH (5 mL) and diethyl ether (10 mL). Single crystals for X-ray diffraction study were obtained by slow diffusion of diethylether into a methanol solution of the complex.

Yield: 0.352 g, 66% (based on Mn(II)). Colour: Red. Elemental analysis data: Anal. (%) Calculated for $[Mn(HL1)(Cl)(CH_3OH)]\cdot 2(CH_3OH)$ $C_{24}H_{30}N_3O_5ClMn$ (530.90 g/mol): C, 54.30; H, 5.70; N, 7.91. Found (%): C, 54.14; H, 5.35; N, 7.63. IR (KBr, ν, cm^{-1}): 3405, 2952, 1610, 1571, 1485, 1353, 1260, 1170, 1080, 984, 960, 560, 450 cm^{-1}. $\square_{eff}$ (B.M)/Mn= 5.42.

2.5 Synthesis of $[Mn(H_2L2)(NCS)_2]$

The ligand H_2L2 (0.354 g, 1 mmol) was dissolved in MeOH (30 mL), $Mn(OAc)_2.4H_2O$ (0.245 g, 1 mmol) was added and followed by addition of NaNCS (0.162 g, 2 mmol). Upon addition of NaNCS, a yellow precipitate formed and the product was collected and washed with diethyl ether (10 mL). Single crystals suitable for X-ray diffraction study were obtained from a slow evaporation of the complex in acetonitrile.

Yield: 0.381 g, 73% (based on Mn(II)). Colour: Yellow. Elemental analysis data: Anal. (%) Calculated for [Mn(H_2L2)$(NCS)_2$] $C_{23}H_{19}N_5O_2S_2Mn$ (516.49 g/mol): C, 53.48; H, 3.71; N, 13.56. Found (%): C, 53.14; H, 3.35; N, 13.10. IR (KBr, ν, cm^{-1}): 3380, 2955, 2072, 1603, 1575, 1470, 1350, 1255, 1165, 1073, 985, 968, 548, 462 cm^{-1}. $□_{eff}$ (B.M)/Mn= 5.51.

3. Results and Discussion

The ligands H_2L1 and H_2L2 were prepared according to reported methods [**22, 23**] by reacting one equivalent of 2,6-diformylpyridine with two equivalents of 2-amino-4-methylphenol or 2-aminophenol in methanol (**Fig. 1**), the yellow products were obtained after stirring for 30 min at room temperature. The ligands are soluble in most organic solvents such as methanol, ethanol, chloroform, dimetylformamide and not soluble in water. Each molecule has two imine groups (C=N) and two 4-methylphenol or benzylalcohol units, one each side of the pyridine. Micro analysis results are given in the experimental section and are in well agreement with the theoretical values. The ^1H spectra of the ligands were also recorded in $CDCl_3$ and both ligands show mirror symmetry in the $CDCl_3$ solution. The ligand H_2L1 was previously synthesised by our group and ^1H NMR data are well agreed with the literature data [**24**]. The ^1H-NMR spectrum of the H_2L2 displays a singlet at □□4.61 ppm corresponding to the protons of the alcohol group protons (Ph-CH_2-O), a singlet at □□8.75 ppm was assigned to azomethine protons (–N=CH–). The aromatic protons were seen at □□7.28-8.17.

The infrared spectra of the free ligands and their Mn(II) complexes were obtained. The infrared spectra of the free ligands were compared with those of the Mn(II) complexes to access the coordination of the ligands to Mn(II) ion. The FT-IR spectra of the Schiff base ligands H_2L1

and H_2L2, the absence of bands due to the aldehyde group ν(C=O) and appearance of a new band at 1620 and 1624 cm^{-1}, respectively, confirming the formation of Schiff base ligands. The azomethine group –CH=N stretching frequencies shifted to lower values in the spectra of the complexes indicating the coordination of azomethine nitrogen to the Mn(II) ion. In the spectra of complex $[Mn(H_2L2)(NCS)_2]\cdot 2(CH_3CN)$, a sharp peak due to thiocyanate stretch was observed at 2072 cm^{-1}.

Thermal studies of the complexes were performed under nitrogen atmosphere in the temperature range of 20–1000 °C. The thermal curves for the complexes are given in the supplementary file (**Figs. S1&S2**) Thermal decomposition of the $[Mn(HL1)(Cl)(CH_3OH)]\cdot 2CH_3OH$ has four decomposition steps all of which are endothermic processes, in the first two steps, about 5% of the mass was lost in the temperature range of 100-300 °C. This loss may be attributed to gradual loss of methanol solvates in the complex. In the third step, approximately 17% of the sample was removed from the structure in the range of 300-500 °C; this was attributed to loss of coordinated chloride ion and methanol molecule. The rest of the organic moiety decomposes gradually up to high temperature leaving metal oxides as a final residue. Chemical structure of complex $[Mn(H_2L2)(NCS)_2]$ was thermally stable up to 270 °C. The complex shows three thermal decomposition steps accompanied with endothermic peaks. In the first two steps, approximately 16.83% and 18.23% of total mass were lost in the temperature range of 270-500 °C. Gradual decomposition of the complex continued up to high temperatures leaving metal oxide as final products.

The magnetic susceptibilities of the complexes were determined using the Evans balance at room temperature [**25**]. The experimental □$_{eff}$ values for the complexes

[Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH) and [Mn(H_2L2)($NCS)_2$] are 5.42 and 5.51 B.M., respectively, within the range of typical high spin d^5 manganese(II) complexes [**26, 16**].

3.1 Molecular structure of [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH)

Red crystals of complex suitable for X-ray diffraction studies were grown from slow diffusion of diethyether into methanol solution of the complex. The complex crystallises as [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH). The structure of the complex was solved in the *orthorhombic* space group *Pbcn*. Molecular structure of the complex with atom numbering is shown in **Fig. 2**. Asymmetric unit of the complex contains mononuclear complex molecule and two methanol solvates. The Mn(II) ion is seven-coordinate with approximate pentagonal bipyramidal geometry, bonded to the pyridinediimine unit and phenolic oxygen atoms (N_3O_2) of the ligand in the pentagonal plane, and to an chloride ion and an oxygen atom of a methanol molecule at the axial positions. Pyridinediimine donors provide angles of 67.96(15)° (N1-Mn1-N2) and 68.75(14)° (N2-Mn1-N3) which are slightly distorted from an ideal value of 72° for a pentagonal plane (**Table 2**).

The manganese(II) complexes reported here structural resemble to the manganese complexes reported in literature [**13-16**]. Seven-coordination in those reported complexes has been ascribed to the macrocyclic nature of the ligand and the stable planarity of the ligand system. Another important factor is that a high spin d^5 ion has no stereochemical preferences.

It is informative to compare the crystal structure of [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH) with the Mn(II) complex of the ligand prepared from 2,6-diformylpyridine and 2-aminophenol. The related Mn(II) complex in the literature was synthesised and structurally characterized by our group [**17**]. In both the complex $[Mn(HL1)(Cl)(CH_3OH)]\cdot2(CH_3OH)$ and the published complex, the Mn(II) ions are seven-coordinate and they both have similar Mn-N(or O) distances. However, the charge of Mn(II) in the complex reported in the literature was balanced by two chloride ions and phenolic oxygen atoms remained protonated. Thus, the complex molecules are not dimerised by Ph-O···H-O-Ph hydrogen bonds as seen in the complex reported here.

In the complex reported in this paper, one of the phenolic OH groups is deprotonated and the other remains protonated. The charge of the complex is then balanced by a chloride anion and one of phenolate groups of the ligand. The proton of phenolic group in the ligand is disordered over two phenolic oxygen atoms. Two complex molecules are dimerized by two component (O-H····O) hydrogen bonds (**Table 3**). Coordinated and non-coordinated methanol molecules are involved in hydrogen bonding with each other linking complex molecules into 1D hydrogen bond chain shown in **Fig. 3**.

In the structure, the two outer rings twisted with respect to the central pyridine ring. The mean planes of C1-C6 and C15/C21 are at 1.619(27) and 12.994(24)° to the central (C9-C14) ring, respectively. There are π-π interactions in the structure stabilising the structure in the solid state. The C12-C15 section of one of the complex molecule is stacked with the C7-C10 section of an adjacent molecule under symmetry operation of 1/2-x, -1/2+y, z. The C14 and C8* atoms are separated by 3.300 Å. The π-π interactions in the structure is shown in **Fig. 4**.

3.2 Molecular structure of $[Mn(H_2L2)(NCS)_2]\cdot2(CH_3CN)$

Yellow crystals of complex suitable for X-ray diffraction studies were grown from slow evaporation of the complex in acetonitrile. The complex was found to crystallise as two acetonitrile solvates per complex molecule. The complex was found to crystallise in the *triclinic* space group *P-1*. The complex molecule shows no crystallography imposed symmetry and molecular structure of the complex with atom numbering is shown in **Fig. 5**. From the X-ray data the imine bond distances (N1-C8 and N3-C14) were found to be 1.2796(16) and 1.2766(16) Å which confirm the double bond character of these bonds (**Table 2**). The structure contains a single seven-coordinate manganese(II) ion that is bound to the N_3O_2 donor set of the pentadentate ligand which forms a pentagonal plane, two thiocyanate ions are bound *via* the nitrogen donor in the axial positions. The angle N4-Mn-N5 is 174.42(4)° and slightly deviated from an ideal value of 180°. This may be due to hydrogen bond interactions of the thiocyanate ions.

The Mn(II) ion has an expected approximate pentagonal bipyramidal geometry where the donors of the pentagonal plane are three pyridine diimine nitrogens and two oxygen atoms. One of the axial thiocyanate ions is hydrogen bonded to one of the OH groups of the ligand (O2-H2···S1) of an adjacent complex molecule and these two concordant hydrogen bonds result in a hydrogen bonded dimer with a $R^2_2(12)$ motif (**Fig. 6**). One of the acetonitrile solvate involves in hydrogen bonding with OH group of the ligand (**Table 3**).

In the structure, the two outer rings considerably twisted with respect to the pyridine ring. The mean planes of C1-C6 and C15/C21 are at 1.619(27) and 12.994(24)° to the central (C9-C14) ring, respectively. There are π-π interactions in the structure stabilizing the structure in the solid state. The C12-C15 section of one of the complex molecule is stacked with the C7-C10 section of an adjacent molecule under symmetry operation of 1/2-x, -1/2+y, z. The C14 and C8* atoms are separated by 3.300 Å.

3.3 UV-Vis. and photoluminescence spectra of the complexes

The UV-Vis absorption spectra of the complexes (10^{-5} M) were investigated in the 250-800 nm range in methanol. The UV–vis spectrum of [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH) shows two absorption maximas at 285 and 520 nm (**Fig. 7**). The band at 285 nm with three consequent shoulders at 315, 350, 390 nm in the spectra may due to π-π* transitions of aromatic groups and azomethine linkage (-C=N-). The absorption at 520 nm with lower intensity can be assigned charge transfer band (M→L). Complex [Mn(H_2L2)($NCS)_2$] exhibits absorption bands at 285 and 420 nm in methanol solution (**Fig. S3**). The bands at 285 with a shoulder at 345 nm can be attributed to the □-□* transitions of the ligand. The band in the 405-420 nm range was assigned to charge transfer transition. No d-d transitions were observed for both complexes at the concentration studied. The single-photon fluorescence spectra of the complexes were collected on a Perkin Elmer LS55 luminescence spectrometer in the solid state. The emission and excitation spectra of [Mn(H_2L2)($NCS)_2$] and [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH) are shown in **Figs. 8&S4**. In the excitation spectra of the complexes, one excitation band was observed in the 585-615 nm range. Upon excitation in the 585-615 nm range, both complexes exhibit only one emission band in the 595-625 nm range in the solid state.

4. Conclusions

In this study, two Mn(II) complexes of pentadentate ligands were successfully prepared and characterized by the spectroscopic and analytic methods. Molecular structure of the complexes was determined by single crystal X-ray diffraction study. The Mn(II) ions in both complexes [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH) and [Mn(H_2L2)($NCS)_2$]·2(CH_3CN) are seven-coordinate with approximate pentagonal bipyramidal geometry. Solid state emission spectra of the complexes shows only one emission band in the 595-625 nm range in the solid state upon excitation in the 585-615 nm range.

Supplementary Information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers for the complexes [Mn(HL1)(Cl)(CH_3OH)].2(CH_3OH) and [Mn(H_2L2)($NCS)_2$].2(CH_3CN) are 1452104 and 1452105, respectively. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 335033; email deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Table 1 Crystallographic data for the complexes.

Identification code	[Mn(HL1)(Cl)(CH_3OH)].2(CH_3OH	[Mn(H_2L2)(NCS)$_2$].2(CH_3CN
Empirical formula	$C_{24}H_{30}Cl\ MnN_3O_5$	$C_{27}H_{25}MnN_7O_2S_2$
Formula weight	530.90	598.60
Crystal size (mm^3)	0.37 x 0.24 x 0.21	0.50 x 0.37 x 0.17
Crystal color	Red	Yellow
Crystal system	*Orthorhombic*	*Triclinic*
Space group	*Pbcn*	*P-1*
Unit cell *a* (Å)	20.290(3)	9.174(3)
b (Å)	12.1646(17)	10.118(3)
c (Å)	20.038(3)	16.052(5)
α (°)	90	78.691(4)
β (°)	90	87.111(4)
γ (°)	90	81.554(4)
Volume (Å3)	4945.9(12)	1444.8(8)
Z	8	2
Abs. coeff. (mm^{-1})	0.682	0.638
Refl. collected	40968	16907
Completeness to □= 28.02°	99.8 %	89.4 %
Ind. Refl. [R_{int}]	5079 [0.0737]	8666 [0.0181]
R1, wR2 [I>2□ (I)]	0.0737, 0.1941	0.0318, 0.0868
R1, wR2 (all data)	0.0910, 0.2036	0.0385, 0.0933
CCDC number	1452104	1452105

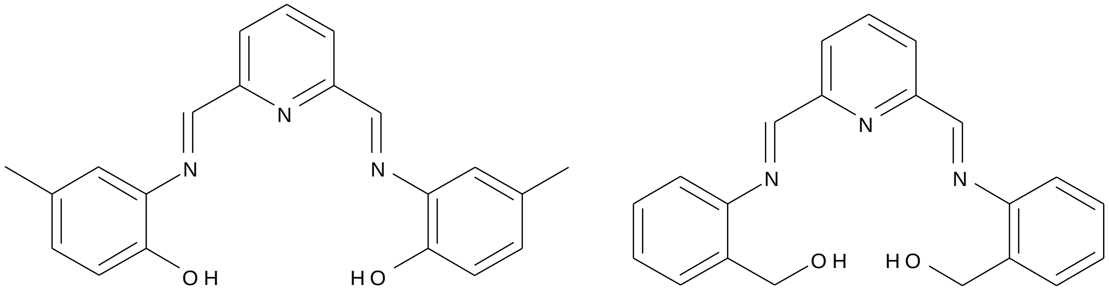
Table 2 Selected bond lengths [Å] and angles [°] for the complexes.

	[Mn(HL1)(Cl)(CH_3OH)].2(CH_3OH)	[Mn(H_2L2)($NCS)_2$].2(CH_3CN)
Mn(1)-N(1)	2.348(4)	2.4577(12)
Mn(1)-N(2)	2.311(4)	2.2839(12)
Mn(1)-N(3)	2.308(4)	2.5299(11)
Mn(1)-O(1)	2.211(4)	2.3404(11)
Mn(1)-O(2)	2.263(3)	2.2529(10)
Mn(1)-O(3)	2.285(4)	-
Mn(1)-Cl(1)	2.5252(16)	-
Mn(1)-N(4)	-	2.1495(13)
Mn(1)-N(5)	-	2.1693(12)
N(1)-Mn(1)-N(2)	67.96(15)	69.34(4)
N(1)-Mn(1)-N(3)	136.41(15)	137.48(4)
N(2)-Mn(1)-N(3)	68.75(14)	68.41(4)
O(1)-Mn(1)-O(2)	81.38(13)	73.23(4)
O(3)-Mn(1)-Cl(1)	177.60(12)	-

N(4)-Mn(1)-N(5)	-	174.42(4)

Table 3 Hydrogen bond parameters [Å and °].

$[Mn(HL1)(Cl)(CH_3OH)].2(CH_3OH)$				
D-H····A	d(D-H)	d(H····A)	d(D····A)	<(DHA)
O1-H1····O1^{i}	0.78 (12)	1.67 (11)	2.448 (7)	169 (17)
O(2)-H(2)····O(2)^{i}	0.82 (12)	1.67 (11)	2.461 (7)	162 (15)
O(3)-H(3)····O(5)	0.79 (7)	1.94 (8)	2.705 (6)	162 (8)
Symmetry transformations used to generate equivalent atoms: i: -*x*+1, *y*, -*z*+1/2 ii: *x*, -*y*, *z*-1/2.				
$[Mn(H_2L2)(NCS)_2].2(CH_3CN)$				
O(1)-H(1C)····N(7)	0.73(2)	2.20(2)	2.922(2)	166(2)
O(2)-H(2)····S(1)^{i}	0.821(19)	2.500(19)	3.2127(12)	145.9(16)
Symmetry transformations used to generate equivalent atoms: i: -x+1,-y+2,-z+1				



H_2L1 H_2L2

Fig. 1 Pentadentate ligands used in this study.

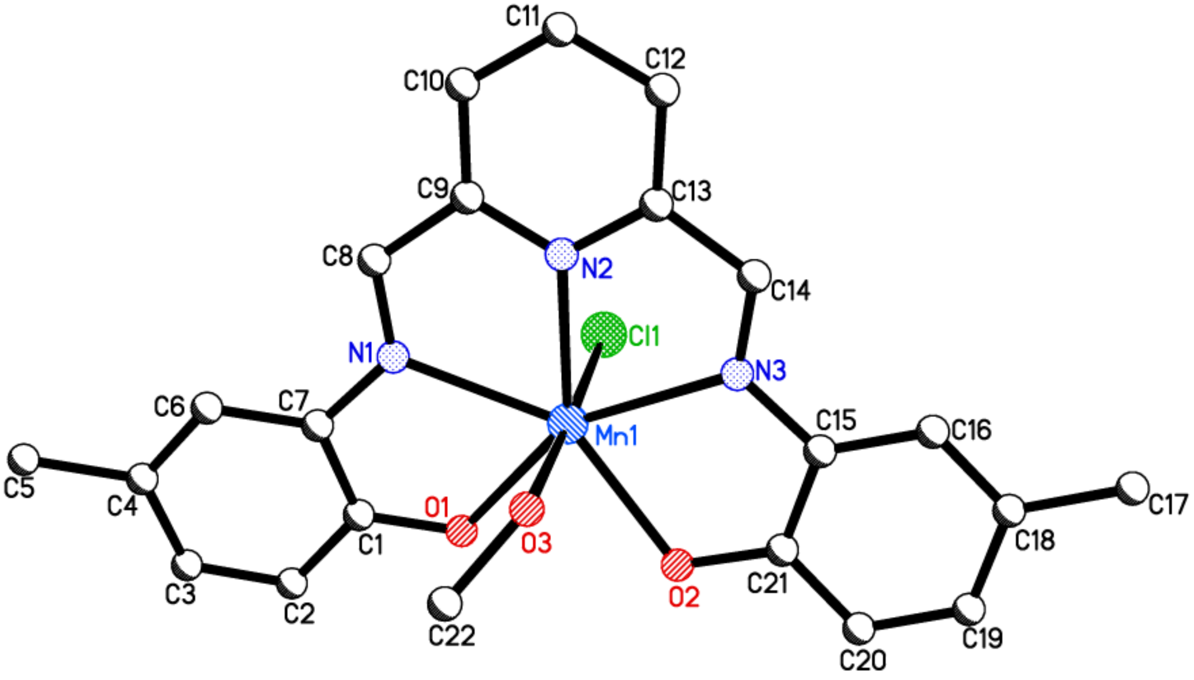


Fig. 2 Molecular structure of complex molecule in [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH), hydrogen atoms and two methanol solvates are omitted for clarity.

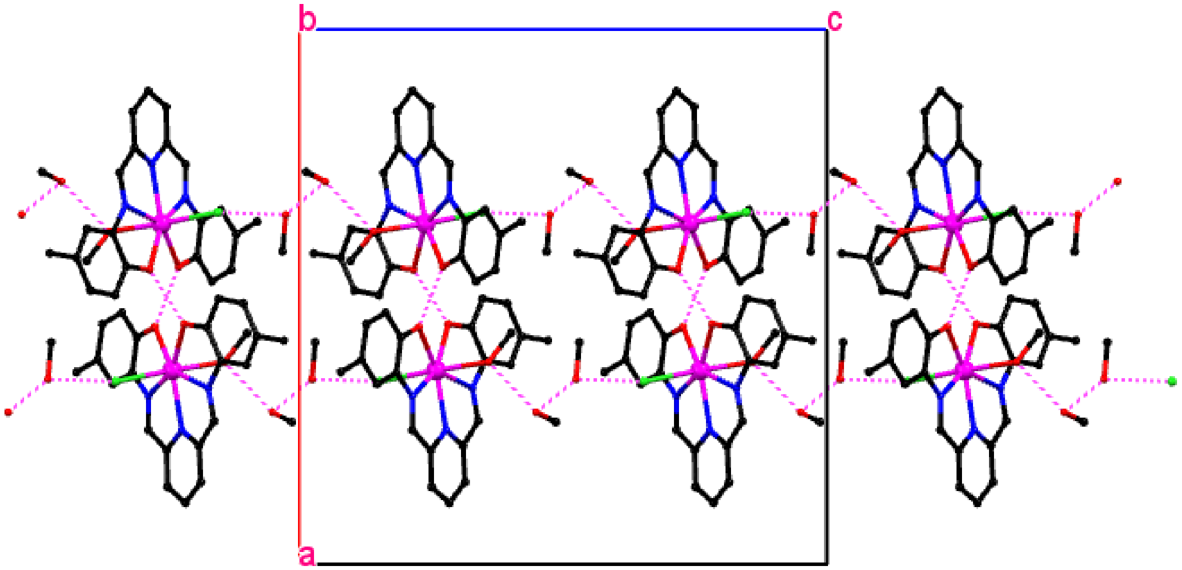


Fig. 3 Packing diagram of [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH) showing hydrogen bonding interactions, hydrogen atoms are omitted for clarity.

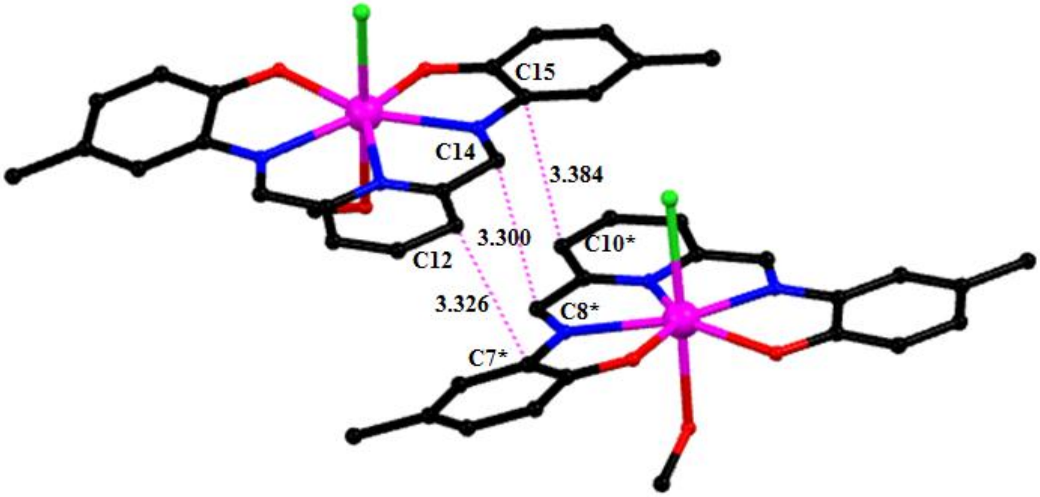


Fig. 4 π-π interactions in [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH), hydrogen atoms are omitted for clarity (symmetry operation* 1/2-x, -1/2+y, z).

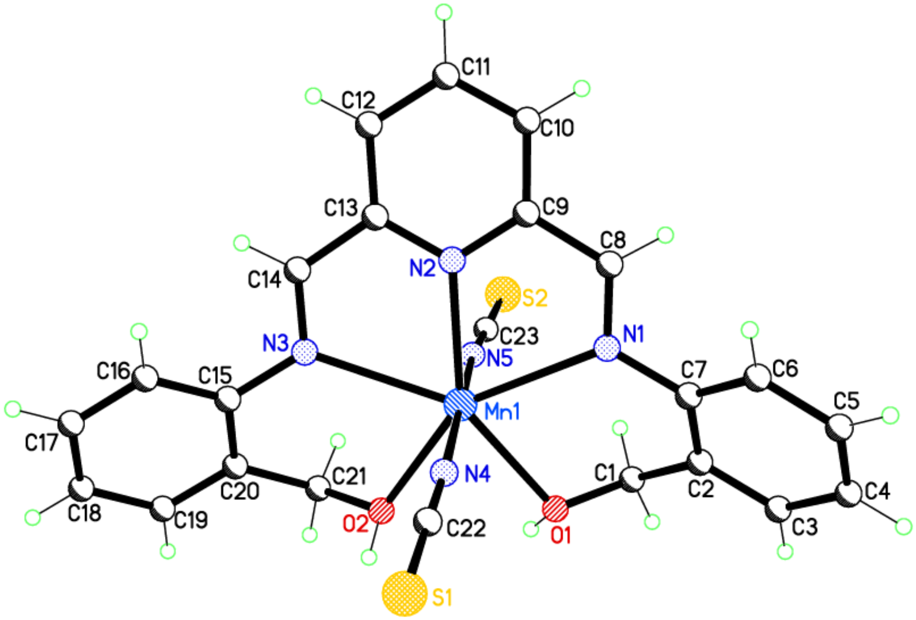


Fig. 5 Molecular structures of complex [Mn(H_2L2)$(NCS)_2$]·2(CH_3CN), two acetonitrile solvates are not shown for clarity.

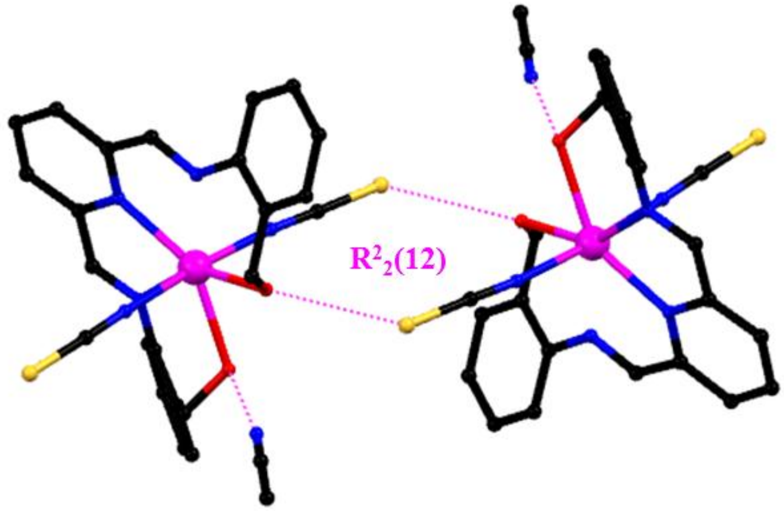


Fig. 6 Hydrogen bonded dimers in $[Mn(H_2L2)(NCS)_2]\cdot 2(CH_3CN)$, hydrogen bonds are shown as dashed lines.

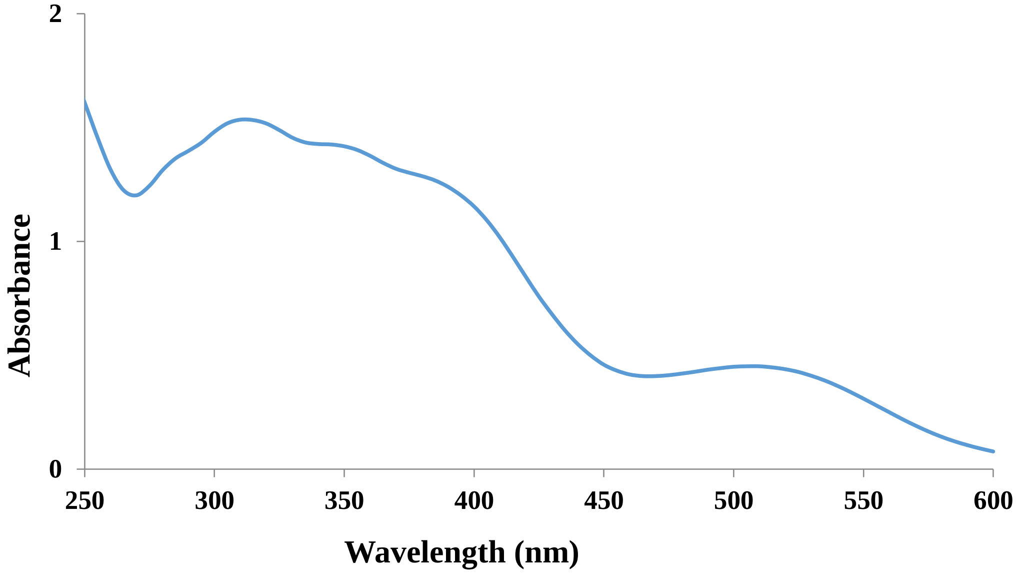


Fig. 7 UV-vis spectrum of [Mn(HL1)(Cl)(CH_3OH)]·2(CH_3OH) in methanol (10^{-5} M).

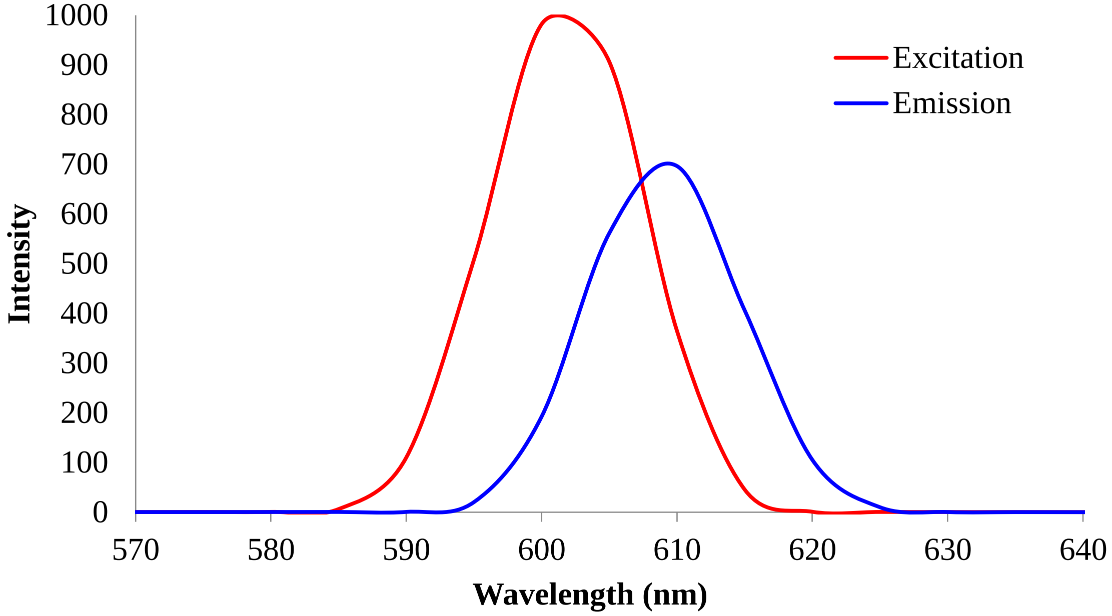


Fig. 8 Excitation and emission spectra of $[Mn(H_2L2)(NCS)_2]$ in the solid state.