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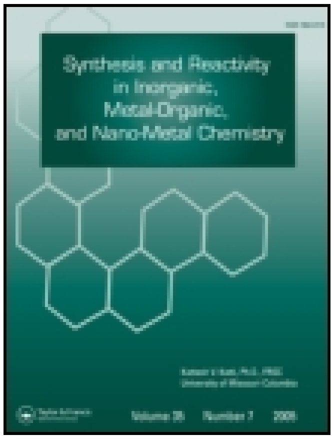

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Spectroscopic Studies and Crystal Structure of Four-Coordinate Manganese(II) Chloride Complex

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Spectroscopic Studies and Crystal Structure of Four-Coordinate Manganese(II) Chloride Complex

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High-spin new, manganese-(II) L_2MnCl_2, complex has been synthesized and its structure was elucidated by using elemental analysis, FT-IR, DTA-TG, ^{1}H-NMR, ^{13}C-NMR, and UV-Visible spectroscopic techniques. The structure of the compound has also been examined crystallographically. The title compound crystallizes in the triclinic space group *P*-1, with unit cell parameters: $a = 11.354(1)$, $b = 11.868(1)$, $c = 12.080(1)$ Å, $V = 1548.9(1)$ Å^3, $D_x = 1.270$ g.cm^{-3}, and $Z = 2$, respectively. The Mn atom was tetra-coordinated to form a distorted tetrahedral geometry by two oxygen atoms of L_2 and two chloride atoms of $MnCl_2.4H_2O$ in the complex.

Keywords crystal structure, DTA-TG, four-coordinated manganese(II), NMR, spectroscopic studies

INTRODUCTION

The compounds of manganese play an essential structural and catalytic role in many proteins. The active Mn sites of many enzymes have been shown to bind with imidazole nitrogen from histidine residues.[1–4] There has been considerable interest in the coordination chemistry of manganese compounds because of their potential utilities as model compounds of manganese containing proteins that exhibit significant involvement of manganese in various biological systems.[5–11] Manganese(II) ion takes usually a high-spin d^5 electronic configuration, which gives no crystal field stabilization energies for any coordination geometries. However, most of the manganese(II) complexes have an octahedral geometry and few examples are known to have the other coordination geometries.

The tautomerism in the Schiff base ligands plays an important role for distinguishing their photochromic and thermochromic characteristics.[12–14] It has been proposed that molecules showing thermochromism are planer, while those showing photochromism are non-planer.[15] However, both appearances being associated with a proton transfer.[16] Therefore the structures of this kind of compounds, which are showed as tautomeric form, are relevant due to the possibility of finding them in the solid state or in solution as ketoamine or phenolimine forms. In the solid state, salicylaldimine compounds tend to form two (N. . .H-O or N-H. . .O) types of hydrogen bonding, respectively.[17–24]

The Schiff bases of 2-hydroxy-3-methoxy-1-benzaldehyde (*o*-vanillin) have been studied previously[25–36] and used as ionophores in a Cu(II) selective electrochemical sensor.[37] These compounds as well as their metal complexes have been found to possess biological activity.[38] Antibacterial activity has also been reported for the ruthenium(II) complex of the Schiff base of 2-hydroxy-3-methoxy-1-benzaldehyde.[39]

In the present study, four-coordinated manganese(II) chloride compound was synthesized (Scheme 1), and then the structure of the compound was enlightened by using data obtained from element analysis, FT-IR, ^{1}H-NMR, ^{13} C-NMR, DTA-TG, and X-ray crystallographic techniques.

EXPERIMENTAL

The ^{1}H-, ^{13}C-NMR spectra were recorded on a Bruker DPX FT-NMR spectrometers operating at 500 and 125.7 MHz. Infrared absorption spectra were recorded on a Perkin-Elmer BX II spectrometer in KBr discs. UV-vis spectra were recorded on a Shimadzu 1201 series spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a LECO CHNS-932 C-, H-, N-analyzer. Melting point was measured on an Electro Thermal IA 9100 apparatus using a capillary tube. The DTA-TG measurements were performed between 25 and 1000°C (in air, rate 10°C/min, Seiko SII TG&DTA 6300). 2-Chlorobenzylamine,

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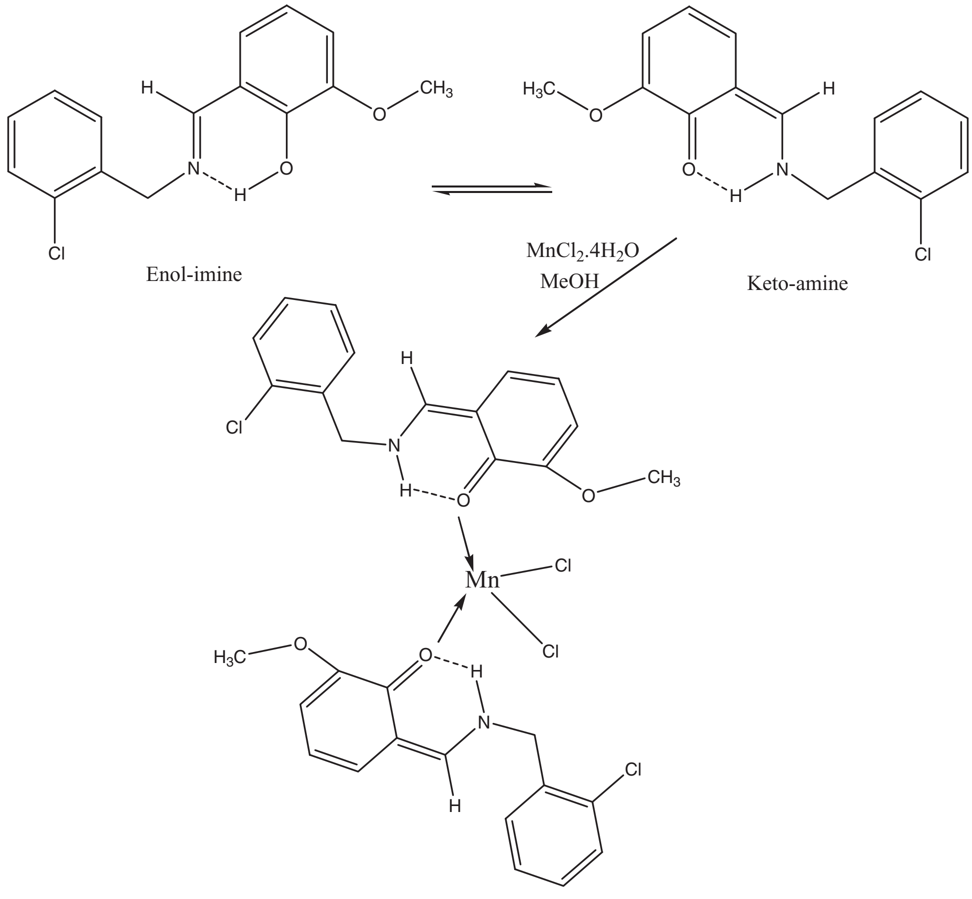


SCH. 1. Synthesis of the Mn(II) complex.

2-hydroxy-3-methoxy-1-benzaldehyde(o-vanillin), THF, DMSO, MeOH, and $MnCl_2.4H_2O$ were purchased from Merck (Germany).

Synthesis of Bis[(*Z*)-6-((2-chlorobenzylamino)methylene)-2-methoxycyclohexa-2,4-dienone] Manganese(II) Chloride

$MnCl_2.4H_2O$ (0,5 g; 2.5×10^{-3} mol) was added to a dry MeOH (100 mL) solution of (*Z*)-6-((2-chlorobenzylamino) methylene)-2-methoxycyclohexa-2,4-dienone[36] (1,39 g; 5.0×10^{-3} mol). The reaction mixture was stirred under reflux for 3 h, then was filtered off, and the filtrate was kept undisturbed for a few days. Bright, red crystalline product was filtered off and washed with methanol and finally was dried in air, m.p. 218–220°C, 1.62 g (95%) yield. Found: C, 53.17; H, 4.13; N, 4.14. Anal. Calcd. for $C_{30}H_{28}Cl_4MnN_2O_4$: C, 53.18; H, 4.14; N, 4.14%. IR (KBr, cm^{-1}): νN-H, 3398 m; νAr-H, 3055 w; νC-H, 2972 w; νC=O, 1653 s; νC=C, 1607 s; νC—N, 1457 s; νAr-O-C, 1232–1213-1170–1053 s; νMn-O, 450 s. ^1H NMR (DMSO): δ ppm, 12.88 (s-broad, 2H, Ar-NH); 6.69 (s-broad, 16H, Ar-H + Ar=CH); 4.21 (s-broad, 4H, $ArCH_2$); 3.28 (s-broad, 6H, OCH_3).

Crystallography

The data collection for the title complex was performed on a STOE IPDS-2 diffractometer employing graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$Å). Data collection, reduction, and corrections for absorption and crystal decomposition were achieved by using X-AREA, X-RED software.[40] The structure was solved by SHELXS-97 and refined with SHELXL-97.[41,42] The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96Å), and refined by using a riding model. All atoms (except hydrogen) were located from a difference Fourier map and refined anisotropically. The details of the X-ray data collection, structure solution and structure refinements are given in Table 1. Selected bond distances and angles are listed in Table 2. The molecular structure with the atom-numbering scheme is shown in Figure 1.[43]

RESULTS AND DISCUSSION

FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV-Visible Spectroscopic, and Thermal studies

The structure of free ligand was studied by using FT-IR, ^{1}H NMR, ^{13}C NMR, UV-vis, and X-ray crystallographic techniques in order to study the hydrogen bonding and tautomeric

TABLE 1
Crystal and experimental data

Formula	$C_{30}H_{28}Cl_4MnN_2O_4$
Formula weight	677.28
Crystal system	Triclinic
Space group	*P*-1
Crystal dimension	0.30 × 0.38 × 0.45 mm^3
Temperature collection	293(2) K
Unit cell parameters	$a = 11.354(1)$Å
	$b = 11.868(1)$Å
	$\beta = 73.975(3)°$
	$c = 12.080(1)$Å
V	1548.9(1)$Å^3$
Z	2
D_c (g cm^{-3})	1.270 g cm^{-3}
μ(MoKα)	0.632 mm^{-1}
F(000)	610
$2\,\theta_{max}$	52.00°
h, k, l range	$-14 \le h \le 14$
	$-14 \le k \le 14$
	$-14 \le l \le 14$
No. of measured reflections	22287
No. of independent reflections	6088
No. of observed reflections	4112
Goodness-of-fit on F^2	1.046
R, R_w ($I > 2\sigma(I)$)	0.051, 0.079
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$	1.326, –0.334 e. $Å^{-3}$

TABLE 2
Some selected bond lengths (Å), bond angles (°), and torsion angles (°)

Mn-O3	2.062(2)	O1-C15	1.426(5)
Mn-O2	2.063(2)	O4-C17	1.369(4)
Mn-Cl2	2.402(1)	O4-C18	1.422(5)
Mn-Cl3	2.405(1)	N2-C23	1.284(4)
Cl1-C1	1.735(4)	N2-C24	1.467(5)
O3-C16	1.302(4)	C6-C7	1.506(5)
O2-C14	1.303(4)	C8-N1	1.293(4)
C9-C14	1.410(4)	N1-C7	1.462(5)
C13-O1	1.373(4)	C24-C25	1.505(5)
O3-Mn-O2	134.9(1)	C16-O3-Mn	125.8(2)
O3-Mn-Cl2	113.2(1)	C14-O2-Mn	125.8(2)
O2-Mn-Cl2	95.9(1)	C13-O1-C15	117.4(3)
O3-Mn-Cl3	94.0(1)	C17-O4-C18	118.7(4)
O2-Mn-Cl3	110.4(1)	C23-N2-C24	125.3(4)
Cl2-Mn-Cl3	106.6(1)	C8-N1-C7	125.4(3)
O2-Mn-O3-C16	78.0(3)	Mn-O3-C16-C17	–23.3(4)
Cl2-Mn-O3-C16	–47.9(3)	C24-N2-C23-C22	177.1(3)
Cl3-Mn-O3-C16	–157.8(3)	C9-C8-N1-C7	178.1(4)
O3-Mn-O2-C14	74.4(3)	Mn-O2-C14-C9	154.1(3)
Cl2-Mn-O2-C14	–154.1(3)	Mn-O2-C14-C13	–26.8(4)
Cl3-Mn-O2-C14	–43.9(3)	C23-N2-C24-C25	–120.4(4)
Mn-O3-C16-C22	157.2(2)	C8-N1-C7-C6	–126.3(4)

equilibrium (enolimine or ketoamine forms) in both the solution and also solid states.[36] UV-vis, ^{1}H NMR, ^{13}C NMR, and X-ray results show that in the solution and solid states free ligand exists in the enolimine form.[36]

The FT-IR spectrum of the compound is given in synthetic procedures (Figure 2). The IR spectra of the metal complex exhibit characteristic changes in the functional group frequencies when compared with the spectrum of the ligand.[36] The OH and C═N vibration band are observed at 3414 and 1635 cm^{-1} of free ligand, respectively. The absorption is not observed in the region of 600–400 cm^{-1} for free ligand. These can be correlated to the specific coordination positions of the ligand. The infrared spectrum shows a band at 3398 cm^{-1} that is assigned to $\nu_{N\text{-}H}$ vibration. In this spectrum, the band characteristic of $\nu_{N\text{-}H}$ is almost unperturbed, indicating that it is not involved in the coordination.[44] The stretching frequency observed at 2835 cm^{-1} in compound shows the presence of N-H. . . .O intramolecular hydrogen bond.[19–20] The C═O bond that is accountable partially for the existence of ketoamine form can also be inferred from the FT-IR spectra of the compound. The compound with strong band at 1653 cm^{-1} possesses highest percentage of ketoamine tautomer due to the stabilization of 2-methoxy-6-methylenecyclohexa-2,4-dienone Ar═O bond. The nonligand IR frequencies observed in the region of 600–400 cm^{-1} are attributed to $\nu_{Mn\text{-}O}$ IR stretching frequencies. The Mn-O strong bond was observed at 450 cm^{-1} for the complex.

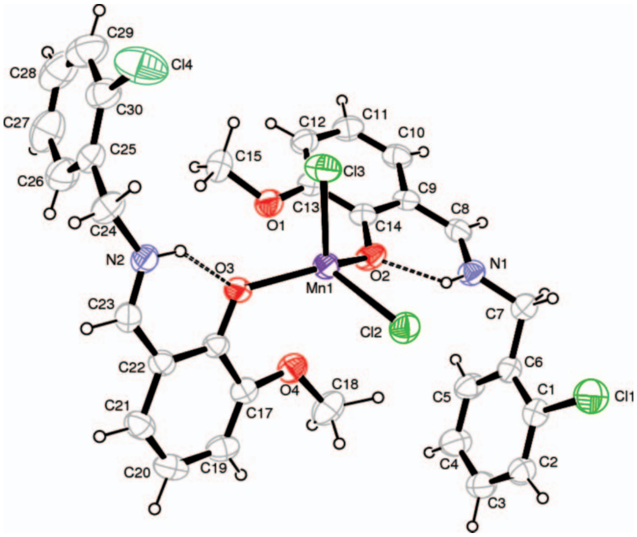


FIG. 1. The molecular structure of the title complex. The intramolecular hydrogen bonds have been indicated by dashed lines (color figure available online).

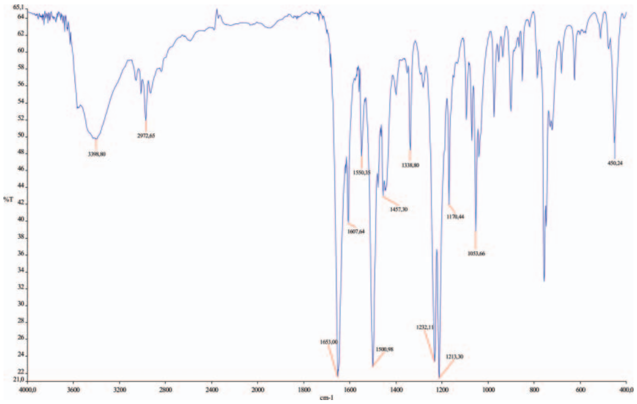


FIG. 2. FT-IR spectrum of the title complex in the solid state (color figure available online).

The ^{1}H NMR data for free ligand show that the tautomeric equilibrium favors the enolimine in $CDCl_3$. The OH and azomethine protons are observed at $\delta = 13.60$ and 8.41 ppm singlets for the free ligand, respectively.[36] The phenyl protons resonate at $\delta = 7.36$, 7.21, 6.94, and 6.79 ppm multiplet, the $ArCH_2$ and OCH_3 protons of the compound gave a singlet at $\delta = 4.87$ and 3.88 ppm for free ligand, respectively. The ^{1}H-NMR data for complex shows that the tautomeric equilibrium favors the ketoamine in DMSO. The N-H proton is observed 12.88 ppm broad-singlet for complex (Figure 3). The azomethine proton is not observed for complex. The phenyl protons resonate at $\delta =$ 6.69 ppm broad-singlet and the Ar = CH protons of the complex gave a broad-singlet at $\delta = 4.21$ ppm. The $ArCH_2$ and OCH_3 protons of the complex are observed a singlet at $\delta = 3.28$ ppm.

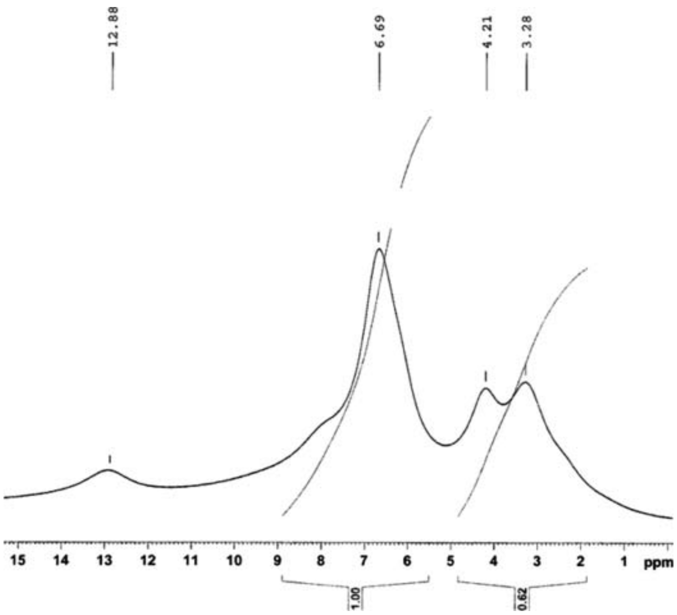
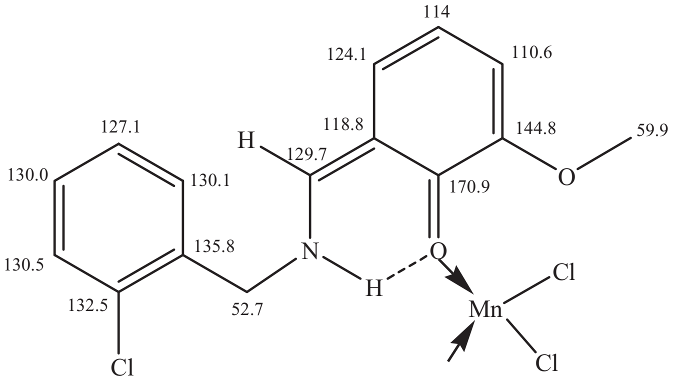


FIG. 3. ^{1}H-NMR spectrum of the title complex.



SCH. 2. ^{13}C-NMR Chemical shifts of the complex in solution media.

According to the ^{13}C-NMR spectra complex has 15 signals (Figure 4). ^{13}C-NMR Chemical shifts are given in Scheme 2 for the complex. The Ar$\underline{C}$-OH carbon is observed at $\delta = 151.6$ ppm for free ligand,[36] while it is observed at $\delta = 170.9$ ppm for the complex. The Ar$\underline{C}$-OH carbon show absorption in the range greater than $\delta = 151.6$ ppm in solution for the complex. It should be pointed out that the high absorption band belongs to the ketoamine form of the Schiff bases with the OH group in the ortho position to the imino group in the solution.

It can be stated as a conclusion that ^{1}H-NMR and ^{13}C-NMR results clearly show the existence of the ligand in the ketoamine form in the complex.

The UV-visible studies of the ligand and complex was done in DMSO solvent (Figure 5). The UV-vis spectrum of the ligand

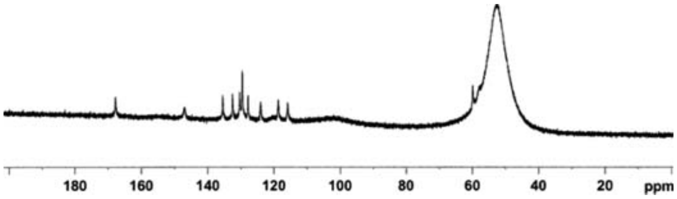


FIG. 4. ^{13}C-NMR spectrum of the title complex.

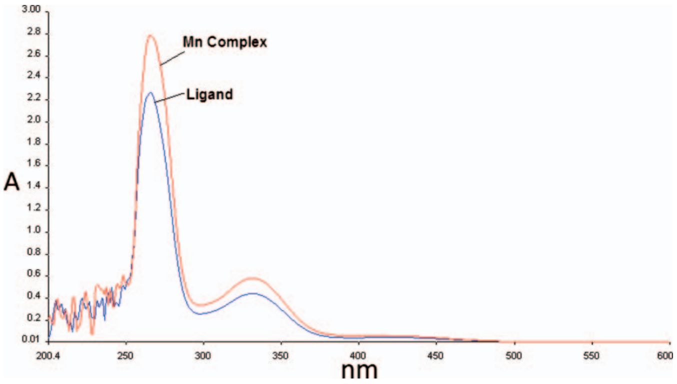


FIG. 5. UV-vis spectrum of the free ligand and its complex in DMSO (color figure available online).

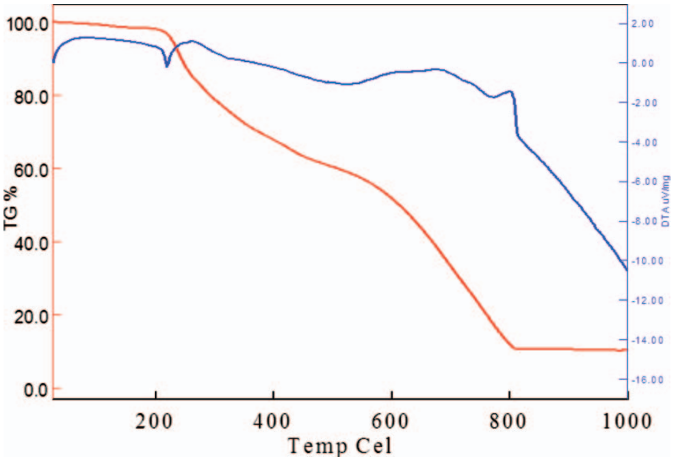


FIG. 6. DTA-TG spectrum of the title complex (color figure available online).

shows only two broad band at 265 nm and 331 nm, which is assigned to the π–$\pi^*$and n–π^* transition of the C=C and C=N. On complexation, these bands are not changed. The complex showed same UV-vis spectrum with the ligand. The complex does not show any d-d transitions but display charge transfer bands at 37735 and 30211 cm^{-1}.

Thermal studies (DTA-TG) of the Mn(II) complex was performed in the temperature range 25–1000°C, at a heating rate of 10°C/min in a air atmosphere (Figure 6). The complex decomposes in two stages. The first step 225–590°C resulted in a mass loss of 45.10%, corresponding to the loss of 2-chlorobenzylamin groups. In the second step, two chloride molecules and aldehyde groups were lost in the 590–900°C range from the Mn(II) complex, with a mass loss of 42.5%. A plateau was obtained after heating above 900°C, which corresponds to the formation of stable MnO_2. The weight of MnO_2 amounted to 12.4%, which shows a good agreement with the metal analysis.

Crystallographic Study

The molecule crystallizes in the triclinic space group. The perspective view of compound together with the atomic numbering scheme is illustrated in Figure 1. The coordination environment about Mn is compressed along the crystallographic *c* axis in such a way that of the O3-Mn-O2 angle is greater and Cl2-Mn-Cl3 angle is shorter than the tetrahedral angle, with values O3-Mn-O2 134.93(11)° and Cl2-Mn-Cl3 106.61(4)°. The remaining O-Mn-Cl angles are less than 100° (O2-Mn-Cl2 95.88(7)° and O3-Mn-Cl3 93.96(7)°).

The central manganese atom is four-coordinated to form a distorted tetrahedral geometry, with two oxygen donors of ligand and two Cl donors of $MnCl_2.4H_2O$. The distances of the two Mn-O bonds are nearly equivalent, being Mn-O3 2.062(2) Å and Mn-O2 2.063(2) Å, within the reported range in polypyridyl Mn(II) complexes.[45] The two Mn-Cl bonds are equivalent, being Mn-Cl2 2.402(1) Å and Mn-Cl3 2.405(1) Å. The ligand coordinates to the Mn(II) center forming a monomember coordination ring.

Intramolecular hydrogen bond occurs between N1-H1. . .O2 [2.584(3) Å] and N2-H2. . .O3 [2.590(3) Å] atoms for the title molecule (Figure 1), respectively. The sum of the Van der Waals radius of the O and N atoms (3.07 Å) is significantly longer than the intramolecular O. . .N hydrogen bond length.[46]

The compounds which have C-N group seem to have a weak electron withdrawing character. Thus, in the title complex, O2-C14 and O3-C16 bond distances of 1.303(4) Å and 1.302(4) Å is also consistent with the C=O double bonding. The C=O bond distance Å indicates the presence of the keto form, with a partial double bond character of the CO group (>C=O ↔C$^+$-O$^-$). X-ray structure determinations reveal that the ketoamine tautomer is favored over the enolimine tautomer for the ligand. This is evident from the observed O-C bond distance of 1.303(4) Å and 1.302(4) Å, which is consistent with the O=C double bond; similarly the N-C distance of N1-C8 1.293(4) Å and N2-C23 1.284(4) Å is also consistent with the N-C single bonding.[36] The ligand exists as dominant form of ketoamines in solid state.

SUPPLEMENTARY MATERIALS

Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository numbers CCDC 691504 & 691505, E-mail: deposit@ccdc.cam. ac.uk.

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