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Hydrogen Bond, π - π , and CH- π Interactions Governing the Supramolecular Assembly of Some Hydrazone Ligands and Their Mn^{II} Complexes – Structural and Theoretical Interpretation

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The hydrazone Schiff base ligands (*E*)-*N'*-(2-hydroxybenzylidene)acetohydrazide (HL¹) and (*E*)-*N'*-(2,3-dihydroxybenzylidene)acetohydrazide (H₂L²) with a functional group variation in the aromatic moiety have been synthesized. The ligands have been used to synthesize the following Mn^{II} complexes: the mononuclear complex [Mn(HL¹)₂]-[ClO₄]₂·2H₂O (**1**), the cocrystallized discrete dinuclear complex {[Mn(HL¹)₂]·[Mn(L¹)₂]}[ClO₄]₂ (**2**), and the phenoxidobridged dinuclear complex [Mn(μ -HL²)(H₂O)]₂[ClO₄]₂ (**3**). The ligands and the complexes were characterized by FTIR

Introduction

Supramolecular chemistry deals with weak and reversible noncovalent interactions between molecules. These forces include hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π - π interactions, CH- π interactions, electrostatic effects, and so on. Supramolecular interactions are demonstrated in molecular self-assembly, peptide folding, molecular recognition, host-guest chemistry, and mechanically interlocked molecular architectures.^[1] Among these weak forces, hydrogen bonding has a significant role in molecular packing for the development of various architectures through crystal engineering.^[2]

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and UV/Vis spectroscopic techniques, and their crystal structures were determined by single-crystal X-ray diffraction analysis. ¹H and ¹³C NMR spectroscopy shows evidence of keto–enol tautomerism of the ligands in solution. All of the compounds develop hydrogen-bonded assemblies of different dimensionalities and architectures. CH– π and π – π interactions also contribute significantly to the overall binding energies of the supramolecular assemblies. The supramolecular interaction energies have been computed at the BP86-D3/def2-TZVPD level of theory.

Hydrogen bonding is the noncovalent interaction between hard acids and hard bases and has a major contribution from electrostatic or Coulombic interactions. Exchange repulsion, polarization energy, charge-transfer energy, covalent bonding, and dispersion forces also contribute to a different extent.^[3] The energy of a hydrogen bond varies from 0.25 to 40 kcal/mol depending on the polarities of the donor and acceptor atoms.^[4] As hydrogen bonds are polar, they are stable in apolar solvents in the absence of competitive hydrogen bonding with the solvent. In contrast to classical hydrogen-bonding interactions, CH- π interactions have been recognized to be the weakest nonclassical hydrogen bond^[5] and contribute significantly in various fields of chemistry such as molecular conformations,^[6] selfassembly,^[7] chiral recognition,^[8] and crystal packing.^[9] CH- π interactions occur between soft acids and soft bases and largely comprise electron correlation energy or dispersion energy. Electrostatic interactions also contribute to a minor extent (ca. 20%).^[10] CH- π interactions are much weaker than conventional H-bonding interactions. Highlevel ab initio calculations for a benzene-methane complex gave a value of -1.45 kcal/mol for the interaction energy, which varies to -5.64 kcal/mol for a benzene-chloroform complex, as the C-H component is significantly activated by three electron-withdrawing groups.^[11] Unlike conventional H bonding, CH $-\pi$ interactions are orientation-independent and persist in highly polar media such as water;

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this is an important criterion when considering the role of CH– π interactions in biological systems.^[12] For π – π stacking interactions, van der Waals dispersion and electrostatic effects have major energetic contributions. In 1990, Hunter and Sanders proposed an electrostatic model of π – π stacking interaction, in which σ – π attraction dominates over π – π repulsion between the stacked arene complexes.^[13]

We have quantitatively explored the role of hydrogen bonding, π - π , and CH- π interactions in the construction of supramolecular assemblies of some acetyl hydrazone ligands (Scheme 1) and their Mn^{II} complexes. Hydrazones are a special class of Schiff bases with additional electrondelocalization stability obtained from the amido fragment (R-CO-NH-) adjacent to the azomethine (-C=N-) chromophore. The N-H proton is very much susceptible to hydrogen bonding and develops interesting supramolecular networks.^[14] In the present work, we have tuned the hydrogen-bonding patterns of two new hydrazone ligands $(HL^1 \text{ and } H_2L^2)$ by increasing peripheral hydrogen-bonding groups. Two Mn^{II} complexes (1 and 2) synthesized with HL¹ under different reaction conditions show distinctly different molecular and supramolecular features. A centrosymmetric dinuclear Mn^{II} complex (3) with H_2L^2 presents symmetrical hydrogen bonding and CH- π interactions to develop three-dimensional supramolecular assemblies. For all of the compounds, the binding energies through supramolecular forces and the individual contributions of each kind of hydrogen-bonding (N-H-O, O-H-O, and C-H···O), π - π , and CH- π interaction to the binding energies have been quantitatively estimated by DFT calculations at the BP86-D3/def2-TZVPD level of theory.



Scheme 1. Outline of the synthesis of HL^1 and H_2L^2 .

Results and Discussion

Synthesis of the Ligands and the Complexes

The ligands HL^1 and H_2L^2 were synthesized as depicted in Scheme 1. Both ligands were obtained in good yield (>80%) in single-crystalline form. For the synthesis of HL^1 , we condensed equimolar amounts of acetic hydrazide and salicylaldehyde. For H_2L^2 , the aromatic aldehyde part is slightly modified with an additional –OH group, that is, acetic hydrazide was condensed with an equimolar amount of 2,3-dihydroxybenzaldehyde. This slight modification of the functional groups in the ligands has a direct effect on their basicity, coordination patterns with metal ions, and the development of supramolecular self-assembly.

Manganese ions can adopt different geometries (such as tetrahedral, square pyramidal, octahedral, and pentagonal

bipyramidal) and oxidation states (+2 to +7) in their complexes, and the geometric and electronic environments of the metal center are strongly dependent on the ligands.^[15] The ligands HL^1 and H_2L^2 can coordinate to metal ions as neutral chelates, monoanionic ketoamines, and dianionic enolimines to stabilize various metal oxidation states, as observed previously with a very similar hydrazone ligand.^[16] We chose manganese for the synthesis of the complexes with the hydrazone ligands HL^1 and H_2L^2 because of their flexibility to render a great variation in geometries, oxidation states, and coordination modes in their resulting complexes; in the present case, we obtained octahedral and pentagonal-bipyramidal Mn^{II} complexes with interesting variations in their supramolecular architectures.

For the synthesis of Mn^{II} complexes with HL¹, the reaction temperature has a major effect on the complex formation. We heated $Mn(ClO_4)_2 \cdot xH_2O$ with HL^1 in a 1:1 methanol/acetonitrile mixture under reflux at 80 °C for 1 h. The slow evaporation of the solution at room temperature (ca. 30 °C) for two weeks resulted in a mixture of singlecrystalline products: plate-shaped single crystals (1) were obtained as the major product and were accompanied by a minor amount of octahedral single crystals (2). Changes to the reaction conditions such as the solvent, temperature, or both did not ensure the exclusive formation of the plateshaped single crystals, whereas the reaction at room temperature (ca. 30 °C) for 0.5 h resulted exclusively in the formation of the octahedral single crystals (2). Single-crystal X-ray diffraction analysis of the plate-shaped crystals revealed a mononuclear octahedral Mn^{II} complex of chemical formula [Mn(HL¹)₂][ClO₄]₂·2H₂O (1), whereas that of the octahedral single crystals from both reactions revealed cocrystallized units of $\{[Mn(HL^1)_2] \cdot [Mn(L^1)_2]\} [ClO_4]_2$ (2). The plate-shaped crystals were carefully isolated mechanically from the mixture, and their purity was not affected in the bulk sample, as observed in the powder diffraction pattern of 1 (Figure S1), in which the resemblance of the experimental pattern with the simulated pattern signifies the homogeneity of the sample. The octahedral crystals of 2 were also isolated in pure crystalline form, as evident from the PXRD pattern (Figure S2). Complex 3 of molecular formula $[Mn(\mu-HL^2)(H_2O)]_2[ClO_4]_2$ was isolated as pure prismatic single crystals by the reaction of $Mn(ClO_4)_2$. xH_2O with H_2L^2 in a 1:1 acetonitrile/2-propanol mixture with gentle heating at 60 °C for 0.5 h followed by slow evaporation for two weeks. The PXRD pattern (Figure S3) confirms the homogeneity of 3. Although all of the complexes contain 1:1 metal-ligand molar ratios, in practice the complexation occurred in the presence of a large excess of Mn^{II} ions, and the Mn^{II}-ligand molar ratios were optimized to 4:1 for the best yields of the complexes.

$^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR Spectra of HL1 and H2L2

The ¹H and ¹³C NMR spectroscopic data of HL¹ and H_2L^2 (Scheme S1) give evidence of keto–enol tautomerism of the ligands in [D₆]dimethyl sulfoxide ([D₆]DMSO) solu-



tion. The ¹H NMR spectra (Figure S4) of both ligands display two sharp singlets at $\delta = 1.95$ and 2.15 ppm, which can be attributed to the methyl protons of the keto and enol forms, respectively. The azomethine proton of the keto and enol forms appears at $\delta = 8.31$ and 8.25 ppm for HL¹ and at $\delta = 8.26$ and 8.23 ppm for H₂L². In the ketoamine forms of both ligands, the NH proton gives a singlet at $\delta =$ 11.6 ppm, whereas the O–H protons of the enolimine forms are recorded as singlets at $\delta = 10.1$ ppm for HL¹ and at 9.1 ppm for H₂L². The keto and enol concentration ratio was estimated to be ca. 3:2 in both ligands from the intensity ratios of the methyl ¹H NMR signals.

The ¹³C NMR spectra (Figure S5) give CH₃ signals at δ = 21.0 ppm for the keto forms and at δ = 22.0 ppm for the enol forms of both HL¹ and H₂L². The C=O carbon atom appears at δ = 166 ppm, whereas its enolic analogue (=C–OH) is recorded at δ = 172 ppm for both ligands. Upon enolization, the azomethine carbon atom undergoes a distinct downfield shift from δ = 141.7 (keto) to 147.0 ppm (enol) for HL¹ and from δ = 142.5 (keto) to 147.7 ppm (enol) for H₂L².

Owing to the presence of a *meta*-OH group in H_2L^2 , the signal of the corresponding aromatic carbon atom is distinctly downfield shifted to $\delta = 146$ ppm compared to that of its unsubstituted analogue HL^1 at $\delta = 116.9$ ppm.

Crystal Structure of HL¹

The single-crystal structure of HL^1 was evaluated to establish its conformation in the metal-free state. The asymmetric unit of the free ligand (Figure 1) reveals that the Schiff base contains three potential donor atoms, that is, a phenolic oxygen atom (O1), an imine nitrogen atom (N5), and a ketonic oxygen atom (O8). The phenolic C2–O1 bond length of 1.353(5) Å is distinctly longer than the ketonic C7–O8 bond length of 1.233(5) Å. From the conformation of the ligand, it is evident that the ONO donor set has a nonchelating orientation.



Figure 1. The asymmetric unit of HL¹.

The crystal packing of HL^1 presents intra- and intermolecular hydrogen-bonding interactions as shown in Figure 2 and listed in Table 1. The phenolic proton associated with O1 is intramolecularly hydrogen bonded to the imine nitrogen atom (N5) to form a stable six-membered ringlike assembly. The amido proton attached to N6 has a favorable orientation for the formation of a cooperative intermolecular hydrogen bond with the ketonic oxygen atom (O8) of the adjacent unit. Thus, a supramolecular centrosymmetric dimer is formed by the $R_2^2(8)$ -type ring assembly between two adjacent molecules.^[17] Adjacent dimers are further connected by another eight-membered ring motif constructed through cooperative C–H···O hydrogen bonding between the ketonic oxygen atom (O8) and one of the methyl protons (H91) to form a one-dimensional cooperative centrosymmetric infinite double-stranded ribbon along the *c* axis. Our group has previously reported the crystal structure of a homologous ligand (HL'),^[16] for which we found a one-dimensional supramolecular single-stranded chain. The free rotation of the amido C–N bond imposes a face-to-face orientation of adjacent molecules in HL¹ and a same-face orientation of adjacent molecules in HL'; thus, the crystal packing of the two homologous ligands is different.



Figure 2. The infinite one-dimensional supramolecular ribbon structure in HL^1 .

Table 1. Hydrogen-bond parameters for the ligands HL^1 and H_2L^2 .

	D–H•••A	d(D–H) [Å]	d(H•••A) [Å]	d(D•••A) [Å]	<(DHA) [°]
HL1	C9–H91···O8	0.978	2.508	3.482(7)	174.0
ЦΙ2	N6–H61···O8	0.885	1.976	2.860(7) 2.640(3)	176.0
11 ₂ L	N3-H31···O1 O2-H21···O1	0.925 0.871	1.960 1.925	2.883(3) 2.757(3)	176.2 159.6

Crystal Structure of H₂L²

The molecular structure of H_2L^2 is shown in Figure 3; H_2L^2 differs from HL^1 by the additional –OH substituent



Figure 3. The asymmetric unit of H_2L^2 .





Figure 4. The two-dimensional array of H_2L^2 viewed along bc plane.

at the *meta* position (C9) of the benzene ring and, hence, contains two potential deprotonation sites (the *ortho* and *meta* OH groups) and can be viewed as a tetradentate ONOO donor ligand.

The hydrogen-bonding features of H_2L^2 are depicted in Figure 4 and listed in Table 1. As observed in the packing of HL^1 , an intramolecular hydrogen bond O8–H81····N4 is formed between the *ortho* OH group and the imine nitrogen atom to form a six-membered ring. The amido proton attached to N3 cooperatively forms an intermolecular hydrogen bond N3–H31···O1 with the ketonic oxygen atom (O1) of an adjacent unit to form a centrosymmetric $R_2^2(8)$ type ring dimer. Four such adjacent dimers are further connected through O8–H81···O1 hydrogen bonds between the *meta* OH group and the ketonic oxygen atom, which acts as a bifurcated H-bond acceptor, to form a helical ring assembly encompassing a void. This ring assembly repeats in the bc plane to develop a two-dimensional undulating array of consecutive left-handed and right-handed helices.

The helical assembly is best viewed in Figure 5, and the space-filling model shows a clear supramolecular void of nanometer dimensions $(1.17 \times 1.28 \text{ nm})$, the maximum distances along the *c* and *b* axes, respectively).

Crystal Structure of [Mn(HL¹)₂][ClO₄]₂·2H₂O (1)

The asymmetric unit of 1 is depicted in Figure 6, and the bond lengths and angles are listed in Table 2. Complex 1 consists of a central Mn^{II} ion coordinated by two neutral



Figure 5. Consecutive left- and right-handed helices in H_2L^2 encompassing a supramolecular void.



Figure 6. Perspective view of the asymmetric unit of 1 with potential hydrogen-bonding groups.



1	2		3		
Bond length					
Mn1–O2 Mn1–O9 Mn1–O16 Mn1–O28 Mn1–N6 Mn1–N25	2.219(2) 2.131(3) 2.209(3) 2.137(3) 2.254(3) 2.239(3)	Mn1–O101 Mn1–N109 Mn1–O113 Mn1–O121 Mn1–N129 Mn1–O132 Mn2–O201 Mn2–O201 Mn2–O212 Mn2–O212 Mn2–O221 Mn2–O232 Mn2–N229	$\begin{array}{c} 2.117(4)\\ 2.256(4)\\ 2.179(4)\\ 2.144(4)\\ 2.254(4)\\ 2.180(5)\\ 2.153(4)\\ 2.267(4)\\ 2.171(5)\\ 2.147(4)\\ 2.147(4)\\ 2.267(4)\end{array}$	Mn1–O2 Mn1–O5 Mn1–O2 Mn1–N11 Mn1–O14 Mn1–O16 Mn1–O17	2.258(3) 2.267(3) 2.125(2) 2.301(3) 2.367(3) 2.205(3) 2.250(4)
Bond angle					
O2-Mn1-O9 O2-Mn1-O16 O2-Mn1-O28 O2-Mn1-N6 O2-Mn1-N25 O9-Mn1-O16 O9-Mn1-O28 O9-Mn1-N6 O9-Mn1-N25 O16-Mn1-O28 O16-Mn1-N25 O28-Mn1-N6 O28-Mn1-N25 N6-Mn1-N25	148.89(9) 103.49(8) 89.14(8) 76.65(8) 92.21(8) 86.03(8) 98.14(8) 73.18(9) 118.87(8) 148.21(9) 93.77(8) 77.19(8) 117.68(8) 73.23(8) 163.77(8)	O132-Mn1-O113 O132-Mn1-N129 O113-Mn1-N129 O132-Mn1-N109 O132-Mn1-N109 O132-Mn1-N109 O132-Mn1-O121 O113-Mn1-O121 N129-Mn1-O121 N109-Mn1-O121 O132-Mn1-O101 O132-Mn1-O101 O132-Mn1-O101 O121-Mn1-O101 O212-Mn2-N209 O212-Mn2-O201 N209-Mn2-O201 O212-Mn2-N229 O201-Mn2-N229 O201-Mn2-O232 N209-Mn2-O232 N209-Mn2-O232 O201-Mn2-O232 N209-Mn2-O232 O212-Mn2-O232 N209-Mn2-O232 O212-Mn2-O232 N209-Mn2-O232 O212-Mn2-O232 N209-Mn2-O232 O212-Mn2-O232 N209-Mn2-O232 O212-Mn2-O232 N209-Mn2-O232 N209-Mn2-O232 O201-Mn2-O231 N209-Mn2-O221 N209-Mn2-O221 N209-Mn2-O221 N209-Mn2-O221 N209-Mn2-O221	$\begin{array}{c} 95.9(2)\\ 72.2(2)\\ 94.0(1)\\ 93.7(2)\\ 71.4(2)\\ 158.9(2)\\ 148.3(1)\\ 96.8(2)\\ 78.0(1)\\ 118.0(2)\\ 95.0(2)\\ 147.8(1)\\ 118.2(2)\\ 77.8(1)\\ 89.5(1)\\ 72.0(2)\\ 150.01(14)\\ 78.1(1)\\ 107.8(2)\\ 174.4(2)\\ 102.2(1)\\ 95.8(2)\\ 102.3(2)\\ 93.1(2)\\ 72.1(2)\\ 96.2(2)\\ 107.4(1)\\ 89.9(1)\\ 89.9(1)\\ 78.2(1)\\ \end{array}$	O2-Mn1-O5 O2-Mn1-O2 O5-Mn1-O2 O2-Mn1-N11 O5-Mn1-N11 O2-Mn1-N11 O2-Mn1-O14 O2-Mn1-O14 O2-Mn1-O14 O2-Mn1-O16 O5-Mn1-O16 O14-Mn1-O16 O2-Mn1-O16 O14-Mn1-O16 O2-Mn1-O17 O5-Mn1-O17 O14-Mn1-O17 O16-Mn1-O17 O16-Mn1-O17 Mn1-O2-Mn1	$\begin{array}{c} 69.8(1)\\ 74.6(1)\\ 144.4(1)\\ 152.9(1)\\ 135.8(1)\\ 79.3(1)\\ 138.4(1)\\ 69.0(1)\\ 146.5(1)\\ 68.5(1)\\ 85.9(1)\\ 86.8(1)\\ 91.2(1)\\ 101.9(1)\\ 86.7(1)\\ 88.8(1)\\ 81.9(1)\\ 97.1(1)\\ 87.3(1)\\ 90.6(1)\\ 168.6(1)\\ 105.4(1)\\ \end{array}$

Table 2. Selected bond lengths [Å] and angles [°] for 1–3.

tridentate ONO donor hydrazone ligands to form an octahedral bischelated complex.

The mean equatorial plane around the central metal ion is formed by two phenoxyl oxygen atoms (O2, O16) and two ketonic oxygen atoms (O9, O28); two azomethine nitrogen atoms (N6, N25) occupy the *trans* (axial) positions to complete the octahedron. The mean planes defined by the donor atoms of the two ligands are almost perfectly orthogonal to each other and are inclined at an angle of 89.13°. The twelve *cis* angles [73.18(8)–118.86(9)°] and three *trans* angles [148.21(8)–163.77(8)°] surrounding the central Mn1 atom show significant deviations from the ideal octahedral bond angles, and the average equatorial bond lengths (2.174 Å) are smaller than the average axial bond lengths (2.247 Å); these deviations indicate a *z*-outtype tetragonal distortion from the ideal octahedral geometry of the central atom. Complex 1 is dicationic, as the ligands coordinate the Mn^{II} ion in a neutral state, and two lattice perchlorate anions counterbalance the +2 charge of the complex.

The crystal packing of **1** reveals that it forms a threedimensional supramolecular network as depicted in Figure 7 from the *ab* and *bc* planes. The hydrogen bonds are listed in Table 3. The intermolecular hydrogen-bonding pattern is centrosymmetric and is assisted by lattice water molecule and percholorate anions. A twelve-membered supramolecular ring motif, expressed as $R^4_4(12)$ in the graph-set notation of Etter,^[17] is formed by the cooperative interaction between pairs of H₂O molecules and ClO₄⁻ ions centrosymmetrically connected by O35–H351···O34 and O35–H352···O32 interactions. Another symmetric $R^2_4(8)$ ring is formed by other pairs of H₂O and ClO₄⁻ ions, which



Figure 7. Three-dimensional supramolecular network in 1 viewed along the (top) ab and (bottom) bc planes.

are cooperatively connected by O42-H421-O41 and O42-H422...O41 interactions. These supramolecular rings interconnect the [Mn(LH)₂]²⁺ units by accepting H bonds from the phenolic oxygen atoms (O2 and O16) and the amido nitrogen atoms (N7 and N26) at the H_2O and ClO_4^- oxygen through ends, respectively, O2–H21···O35, 016-H161---O42, N7-H71---O32, and N26-H261---O37 interactions. This network is further supported by weak C10-H101----O33, C10--H102---O39, and C10–H103····O37 hydrogen bonds between the methyl protons attached to C10 of the ligand and three ClO_4^- oxygen atoms to expand the three-dimensional supramolecular network.

Crystal Structure of $\{[Mn(HL^1)_2] \cdot [Mn(L^1)_2]\}[ClO_4]_2$ (2)

The asymmetric unit of 2 is depicted in Figure 8, and the bond parameters are listed in Table 2. The complex contains two molecules of octahedral Mn^{II} bischelates with HL¹ connected through hydrogen bonds.

One of the cocrystallized molecules (Mn1 center) is dicationic, as both ligands are in their neutral state, whereas the other (Mn2 center) is neutral, as both ligands are in their monoanionic state. In both molecules, the mean basal planes of the octahedra are formed by two ketonic oxygen atoms and two phenoxyl oxygen atoms, whereas the axial



Table 3. Hydrogen-bond parameters for 1-3.

	D–H···A	d(D–H) [Å]	<i>d</i> (H … A) [Å]	d(D•••A) [Å]	<(DHA) [°]
1	O2–H21…O35	0.860	1.740	2.596(4)	174.5
	N7-H71···O32	0.890	2.020	2.890(5)	168.7
	O16-H161-O42	0.840	1.760	2.599(5)	173.6
	N26-H261O37	0.880	2.050	2.921(5)	169.6
	O35-H351O34	0.830	2.060	2.890(5)	174.1
	O35-H352···O32	0.820	2.200	2.971(5)	156.9
	O42-H421···O41	0.830	2.280	2.943(7)	137.8
	O42-H422····O41	0.820	2.300	3.048(7)	151.7
	C10-H101-O33	0.954	2.555	3.475(5)	162.0
	C10-H102-O39	0.949	2.497	3.435(5)	169.9
	C10-H103O37	0.958	2.592	3.426(5)	145.7
2	N210-H2101-O305	0.867	2.183	3.028(9)	164.7
	N110-H1101-O303	0.868	2.014	2.868(9)	167.9
	O101-H1011···O201	0.835	1.619	2.435(9)	165.1
	N230-H2301-O403	0.877	2.065	2.881(9)	154.6
	N130-H1301-O503	0.869	1.992	2.826(9)	160.5
	O121-H1211···O221	0.960	1.519	2.440(9)	159.2
	C112-H1121····O402	0.957	2.272	3.218(9)	169.8
	C133-H1333···O502	0.955	2.460	3.356(9)	156.0
	C213-H2131···O304	0.960	2.439	3.355(9)	159.5
	C233-H2333····O402	0.986	2.298	3.157(9)	145.1
3	O17-H171····O22	0.835	2.305	3.012(6)	142.6
	O17-H172···O20	0.842	2.007	2.807(6)	158.3
	O16-H162····O14	0.816	2.091	2.811(6)	147.0
	O5-H51···O19	0.819	1.971	2.781(6)	169.8
	N12-H121-O21	0.875	2.222	3.077(6)	165.7

positions are occupied by the azomethine nitrogen atoms. The average Mn–N bond lengths [2.255(4) and 2.267(4) Å in the Mn1 and Mn2 units, respectively] are distinctly longer than the average Mn–O bond lengths [2.155(4) and 2.154(4) Å in the Mn1 and Mn2 units, respectively], which



Figure 8. Asymmetric unit of 2 with hydrogen-bond origins.

indicates a *z*-out-type tetragonal distortion in both units. The disordered perchlorate molecules with Cl401 and Cl501 have 50% occupancy in the lattice for each complex unit. The oxygen atoms O404 and O405 are always present and belong solely to either Cl401 or Cl501, whereas the other oxygen pairs (O402/O403 and O502/O503) appear according to the occurrence of Cl401 and Cl501, respectively.

The hydrogen-bonding features of 2 are evident from Figure 8 and are listed in Table 3. The cationic and neutral units of the complex are connected through the phenolic oxygen atoms, which are involved in O101-H1011...O201 and O121-H1211...O221 hydrogen bonds. Each of the



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Figure 9. Supramolecular packing in 2 viewed along the (left) a and (right) c axes. Hydrogen atoms not involved in H bonds are omitted for clarity.



amido N-H groups makes intermolecular bonding through N110-H1101-O303, N210-H2101-O305, N130-H1301-O503, and N230-H2301-O403 interactions with perchlorate oxygen atoms. The perchlorate oxygen atoms also accept hydrogen bonds from the methyl carbon atoms to form weak intermolecular C112-H1121-O402, C133-H1333---O502. C213-H2131---O304. and C233-H2333---O402 hydrogen bonds. Thus, a three-dimensional supramolecular network connected by the lattice perchlorate ions is formed, as depicted in Figure from two different planes.

Crystal Structure of $[Mn(\mu-HL^2)(H_2O)]_2[ClO_4]_2$ (3)

Complex 3 is a centrosymmetric dimer consisting of heptacoordinate Mn^{II} ion, a phenoxido-bridging hydrazone ligand, and an axial H₂O ligand, as depicted in Figure 10. The important bond parameters are listed in Table 2. Although the ONOO donor hydrazone ligand contains two potential deprotonation sites (the *ortho* and the *meta* phenoxyl groups), the ortho phenoxyl oxygen is deprotonated and acts as a bridge between two centrosymmetric Mn^{II} ions, which are separated by 3.488 Å. A similar dimeric complex of a homologous hydrazone ligand reported by Ray et al.^[18] is a phenoxido-bridged non-centrosymmetric Mn^{II}-hydrazone dimer that provides a similar chelate environment as that observed in 3. The hydrazone ligand provides a pentagonal base constructed of the ketonic oxygen atom (O14), imino nitrogen atom (N11), two bridging ortho-phenoxido oxygen atoms (O2) from two cooperating ligands, and the meta phenoxyl oxygen atoms (O5). The pentagonal bipyramid is completed by the axial coordination of two water molecules. Complex 3 contains a NO_6 chromophore around the metal ions and differs significantly from the previously reported complex; the axial ligands render 3 centrosymmetric but make the previously reported complex non-centrosymmetric, as the axial positions are occupied by many different ligands such as N_3^- , H₂O, and MeOH to provide a N₂O₅ chromophore around



Figure 10. The centrosymmetric dimeric molecule of **3** with potential hydrogen-bonding groups.

the metal centers. The average Mn–O bond length (2.254 Å) in the basal plane, the Mn–N_{imine} bond length (2.301 Å), and the Mn–O–Mn bond angle (105.4°) in **3** are in good agreement with those in the previously reported complex.

The supramolecular features of **3**, as depicted in Figure 11 and listed in Table 3, are more extensive than those in the previously reported complex.^[18] A centrosymmetric $R_4^{4}(12)$ -type supramolecular ring is formed by one of the H₂O ligands (O17) and the lattice perchlorate anion from two adjacent molecules through O17–H171···O22 and O17–H172···O20 connections and is additionally supported by the O5–H51···O19 chain. Along the *bc* plane, the ring is further connected to two other neighboring molecules through a N12–H121···O21 chain involving the amido N–H groups of the ligand and one of the perchlorate oxygen atoms (O21; Figure 11 top).

The other H_2O ligand (O16) forms a cooperative hydrogen bond O16–H162···O14 with the ketonic oxygen atom (O14) of an adjacent molecule in the *ac* plane (Figure 11 bottom). Thus, a symmetrical three-dimensional supramolecular network is constructed.

The three-dimensional molecular packing is further supported by a pair of CH– π interactions between each neighboring molecule stacked parallel along the *a* axis (Figure 12). The distance between the methyl proton (H152) and the aromatic ring centroid is very short (2.732 Å) and agrees well with those of other reported complexes in which CH– π interactions play an important role in structural orientation.^[19] The roles and magnitudes of the intermolecular interactions as quantified through theoretical calculations are discussed below.

Fourier-Transform Infrared Spectra

The IR spectra of 1–3 were analyzed and compared with those of the free ligands (HL¹ and H₂L²) in the $\tilde{v} = 4000$ – 400 cm^{-1} region. In the IR spectra of the free hydrazone ligands (Figures S6 and S7 for HL¹ and H₂L², respectively), the imine stretching bands appeared at $\tilde{v} = 1601$ and 1600 cm⁻¹ for HL¹ and H₂L², respectively, but the observation of the characteristic imine bands for the complexes at lower stretching frequencies of $\tilde{v} = 1548$, 1559, and 1567 cm⁻¹ for 1–3, respectively (Figures S8–S10), indicates the coordination of the imine nitrogen atom to the metal center.^[20,21] The $v_{C=O}$ signals for the amide moieties (-CONH-) are centered at $\tilde{v} = 1669$ and 1654 cm⁻¹ for HL¹ and H_2L^2 , respectively, and undergo shifts to lower frequencies of $\tilde{v} = 1605$, 1596, and 1615 cm⁻¹ in the respective complexes 1-3. The marginal shifts of the broad N-H stretching bands from $\tilde{v} \approx 3100 \text{ cm}^{-1}$ in the spectra of the ligands to $\tilde{v} = 3076$ and 3084 cm⁻¹ for 1 and 2 suggests the presence of hydrogen-bonded non-coordinated amine groups. The N–H stretching band in the spectrum of 3 falls in the very broad and overlapping region of $\tilde{v} = 3600$ - 3000 cm^{-1} , which has contributions from several O–H stretching vibrations. The coordination of the ligand to the metal center is further substantiated by prominent Mn-N





Figure 11. Three-dimensional supramolecular network in 3 viewed along the (top) bc and (bottom) ac planes.

stretching bands at $\tilde{v} = 432$, 415, and 421 cm⁻¹ in the spectra of **1–3**, respectively.^[22] Generally, hydrogen-bonded alcoholic O–H bond stretches are found in the range $\tilde{v} = 3600-3200$ cm⁻¹, and these bands are not very well documented in the spectra of the ligands. For the present complexes, the broad bands at $\tilde{v} \approx 3240$, 3227, and 3295 cm⁻¹ for **1–3**, respectively, are attributed to the phenolic O–H bonds coordinated to the metal centers and also participating in hydrogen bonding. Very broad bands in the range $\tilde{v} = 3600-3400$ cm⁻¹ for **1** and **3** confirm the presence of water molecules involved in hydrogen bonding.^[23] The character-

istic stretching bands of the perchlorate anions appeared at $\tilde{\nu} \approx 1100 \text{ cm}^{-1}$ in the spectra of all three complexes.

Electronic Spectra

The electronic spectra of 1–3 in HPLC-grade acetonitrile solvent were analyzed and compared with those of the free ligands (HL¹ and H₂L²) in the region $\lambda = 800-200$ nm. The UV/Vis spectra of the Schiff base ligands exhibit two intense absorption bands at $\lambda = 287$ and 318 nm for HL¹ and





Figure 12. CH– π interactions in **3** [Å].

 $\lambda = 292$ and 329 nm for H₂L², which can be attributed to $\pi \rightarrow \pi^*$ (C=N) and $n \rightarrow \pi^*$ transitions. Three distinct absorption bands appeared in the spectra of the complexes at $\lambda = 287$, 318, and 365 nm for 1, $\lambda = 289$, 322, and 366 nm for 2, and $\lambda = 310$, 356, and 385 nm for 3. The high-energy bands at $\lambda = 287$, 289, and 310 nm for 1–3, respectively, originate from $\pi \rightarrow \pi^*$ transitions of the aromatic rings. Intraligand $n \rightarrow \pi^*$ charge-transfer bands appeared at $\lambda = 318$, 322, and 356 nm for 1–3, respectively. It is quite reasonable to assign the broad bands in the region $\lambda = 350$ –370 nm in the spectra of 1–3 to ligand-to-metal charge transfer (LMCT) from the Schiff base ligand to the Mn^{II} center.

Theoretical Calculations of Weak Interactions

We have divided the theoretical study into two parts. In the first part, we have analyzed the solid-state structures of the ligands (HL¹ and H₂L²) and focused our attention on the strong influence of the additional phenolic group in H₂L² on the crystal packing. Secondly, we have studied some interesting noncovalent interactions in the manganese complexes with special interest in the π - π stacking interactions that are established between positively charged moieties.



Figure 13. Partial views of ligands HL^1 and H_2L^2 (distances in Å).

The distinct difference between the HL¹ and H₂L² ligands is the presence of an additional phenolic OH group in the latter. This additional group has a strong influence on the solid-state packing. Ligand HL¹ forms an infinite planar ribbon stabilized by a hydrogen-bonding network (see Figure 13, left). The network consists of the combination of a double and strong N–H···O=C hydrogen bond (1.98 Å) involving the amido group with a double and weaker C–H···O=C hydrogen bond (2.51 Å). In contrast, H₂L² (Figure 13, right) does not form an equivalent combination of hydrogen bonds owing to the presence of the additional OH group. This group establishes a hydrogen-bond interaction with the amido C=O group instead of the double C–H···O=C hydrogen bond observed in HL¹.

We have evaluated energetically these hydrogen-bonding interactions to investigate if the single O-H···O=C hydrogen bond in H_2L^2 compensates the double C-H···O=C hydrogen bond observed in HL¹. The interaction energies are shown in Figure 14. From the inspection of the results, several interesting points arise. First, the strength of the double N-H···O=C hydrogen bond is large and similar in both ligands. It is slightly more favorable in H_2L^2 , in agreement with the experimental hydrogen-bonding distances. Second, the double C-H···O=C hydrogen bond is weak, as the interaction energy ΔE_1 is only -3.7 kcal/mol owing to the very low acidity of the hydrogen atoms. However, the single O-H···O=C hydrogen bond in H₂L² has $\Delta E_3 = -$ 7.1 kcal/mol, which clearly compensates the double C-H···O=C hydrogen bond in HL¹. This energetic difference is responsible for the completely different architecture observed for H_2L^2 in the solid state.

The second part of the theoretical study is devoted to the analysis of the π - π stacking interactions in 1, in which both aromatic rings belong to positively charged moieties. Moreover, we have compared its solid-state structure to that of 2 and focused our attention on the crucial role of the water molecules that are present in 1 and absent in 2. In Figure 15, we present a partial view of the crystal structures.



Figure 14. Interaction energies of several hydrogen-bonded dimers retrieved from the solid-state structures of HL^1 and H_2L^2 .



Figure 15. Partial view of intermolecular interactions in 1 and 2 (distances in Å).

In 1, four water molecules form strong hydrogen bonds (1.74–1.76 Å) with four OH groups in which the acidity of the hydrogen atom is enhanced by the coordination of the oxygen atom to the Mn^{II} ion. Moreover, a π - π stacking

interaction (centroid to centroid distance 3.83 Å) is also formed between adjacent complexes. In contrast, **2** does not form the stacking interaction. The absence of water molecules in **2** and the presence of protonated and deprotonated L¹ ligands facilitate the formation of intermolecular O···H–O hydrogen bonds to generate a more compact crystal structure.

In Figure , we show the different theoretical models used to analyze energetically the different interactions observed in **1** and **2**. For **1** (Figure 16, left), we have computed the interaction energy of the π - π assembly (without considering the counterions), and it is very unfavorable because of electrostatic repulsion ($\Delta E_5 = 127.6$ kcal/mol) between each Mn^{II} complex, which has two positive charges. However, the binding energy of this assembly ($\Delta E_6 = -75.4$ kcal/mol) for the neutral system (that is, with two perchlorate anions included for each Mn^{II} complex) is very favorable. Therefore, the analysis of weak interactions such as π - π stacking



Figure 16. Intermolecular interaction energies retrieved from the solid-state structures of 1 and 2.



Figure 17. Interaction energies of a self-assembled dimer of 3 (left) and a theoretical model of this dimer in which one coordinated water molecule has been eliminated (right; distances in Å).

in the presence of strong electrostatic interactions between counterparts should be carefully performed. In contrast, the supramolecular assembly in **2** (Figure 16, right) presents a very favorable interaction energy ($\Delta E_7 = -98.1$ kcal/mol) without consideration of the effect of the counterions, because one Mn complex is neutral. Interestingly, the absence of water molecules in the crystal structure of **2** allows the formation of a very strong assembly between the neutral and charged Mn^{II} complexes through two strong hydrogen bonds.

Finally, we have analyzed the dimer in 3 (Figure 17), for which two interesting C-H··· π interactions are established in addition to the strong hydrogen-bonding interactions. It should be mentioned that the C–H··· π distance is very short (2.73 Å, see Figure 17) compared to those previously reported for this type of interaction.^[24] To evaluate the contribution of this interaction to the binding energy, we have computed two theoretical models. The first one corresponds to the self-assembled dimer found in the crystal structure, and the dimerization energy is $\Delta E_8 = -27.2$ kcal/mol. This binding energy corresponds to both the hydrogen-bonding and C–H··· π interactions. We have also computed a hypothetical dimer in which the coordinated water molecule that participates in the hydrogen-bonding interaction has been eliminated. For this dimer, the binding energy is reduced to $\Delta E_9 = -12.8$ kcal/mol, which corresponds to the contribution of both C–H··· π interactions. Therefore, each interaction contributes -6.4 kcal/mol, which is larger in absolute value than commonly reported for C–H··· π complexes^[25] and agrees with the very short C–H··· π distance observed in the solid-state structure of 3. This large interaction energy value is likely due to the electron-rich nature (π -basicity) of the aromatic ring.

Conclusions

We have reported three new Mn^{II} coordination complexes (1–3) synthesized from two different acetylhydrazone Schiff base ligands, HL^1 and H_2L^2 . The ligands establish a keto–enol tautomerization equilibrium in solution but exist solely in the keto form in the solid state and develop supramolecular assemblies assisted by N–H···O, O–H···O, and C-H···O hydrogen bonding. The Mn^{II} complexes consist of dicationic metal-ligand chelate units, as HL^1 (in 1 and 2) and H_2L^2 (in 3) behave as neutral ligands. Two ClO_4^- ions counterbalance the dicationic complex. Lattice water molecules in 1 and 3 help to stabilize the molecular assemblies through hydrogen bonding. In 2, owing to the absence of lattice H₂O molecules, the supramolecular stabilization is achieved through the cocrystallization of a neutral complex unit in which HL¹ undergoes deprotonation and behaves as an anionic ligand. Thus, all of the complexes form threedimensional supramolecular networks. The crystal packing of 3 is supported by significant C-H··· π interactions between two adjacent coplanar units. Theoretical calculations have been performed to estimate the binding energies of the molecules and the individual contributions of each noncovalent interaction. The C–H··· π interaction in 3 is among the highest reported dispersion forces.

Experimental Section

General Remarks: The FTIR spectra of the compounds were recorded with a Perkin–Elmer RX I FTIR spectrometer with samples as KBr pellets in the range $\tilde{v} = 4000-400 \text{ cm}^{-1}$. The electronic spectra were recorded in the range $\lambda = 800-200 \text{ nm}$ at 300 K with a Perkin–Elmer Lambda 40 (UV/Vis) spectrometer with HPLC-grade acetonitrile as the solvent. The ¹H NMR spectra of the Schiff base ligands were recorded with a Bruker 400 MHz FT-NMR spectrometer with trimethylsilane as an internal standard and samples in [D₆]DMSO solvent. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a PANalytical Empyrean X-ray powder diffractometer with Cu- K_a radiation.

Theoretical Methods: The energies of all the complexes included in this study were computed at the BP86-D3/def2-TZVPD level of theory by using the crystallographic coordinates within the program TURBOMOLE version 6.4.^[26] For the calculations, we have used the BP86 functional with the latest available correction for dispersion (D3).^[27]

Chemicals: Solvents in anhydrous form were purchased from commercial suppliers. Acetic hydrazide, salicylaldehyde, and 2,3-dihydroxybenzaldehyde were purchased from Aldrich Chemical Company and used as received. Manganese perchlorate salt was prepared by the standard procedure.^[28]



Caution! Perchlorate salts are potentially explosive and should be used in small quantities and with much care, although no harm was caused during the present experiments.

Hydrazone Ligand HL¹: The ligand HL¹ [(E)-N'-(2-hydroxybenzylidene)acetohydrazide] was prepared by the condensation of acetic hydrazide (0.74 g, 10 mmol) with salicylaldehyde (1.221 g, 10 mmol) in methanol (100 mL). The methanolic solution was heated under reflux at 65 °C for 5 h, and a colorless solution was obtained. The solvent was removed under reduced pressure, and the white residue was purified by recrystallization from methanol to afford colorless shiny crystals, yield 0.155 g (87%). FTIR (KBr): $\tilde{v} = 1601 [v(C=N)], 1669 [v(C=O)] cm^{-1}. UV/Vis: \lambda_{max} = 287$ $(\pi \rightarrow \pi^*)$, 318 $(n \rightarrow \pi^*)$ nm. ¹H NMR (400 MHz, [D₆]DMSO): $\delta =$ 1.95 (s, 3 H, CH₃, keto), 2.15 (s, 3 H, CH₃, enol), 6.86 (m, 1 H, Ar), 7.22 (m, 1 H, Ar), 7.46 (d, 1 H, Ar), 7.59 (d, 1 H, Ar), 8.31 (s, 1 H, CH, keto), 8.25 (s, 1 H, CH, enol), 11.2 (s, 1 H, Ar OH), 11.6 (s, 1H, NH keto), 10.1 (s, 1 H, OH enol) ppm. ¹³C NMR $([D_6]DMSO): \delta = 21.0 (CH_3, keto), 22.0 (CH_3, enol), 166.1 (C=O)$ keto), 172.2 (C-OH enol), 141.7 (CH keto), 147.0 (CH enol), 116.8, 119.2, 119.9, 127.5, 131.5, 157.0 (Ar keto), 117.0, 120.6, 120.1, 130.2, 131.8, 158.0 (Ar enol) ppm.

Hydrazone Ligand H₂L²: The ligand H₂L² [(*E*)-*N'*-(2,3-dihydroxybenzylidene)acetohydrazide] was prepared by the condensation of a methanolic solution (100 mL) of acetic hydrazide (0.74 g, 10 mmol) with 2,3-dihydroxybenzaldehyde (1.381 g, 10 mmol) to form a light yellow solution upon heating overnight under reflux at 65 °C; from the solution, a white solid precipitated. The white solid was collected by filtration and redissolved in warm MeOH. On slow evaporation of the solvent, shiny colorless crystals of H₂L² were obtained, yield 0.161 g (83%). FTIR (KBr): $\tilde{v} = 1600$ [v(C=N)], 1654 [v(C=O)] cm⁻¹. UV/Vis: λ_{max} = 292 (π→π^{*}), 329 (n→π^{*}) nm. ¹H NMR (400 MHz, [D₆]DMSO): δ 1.95 (s, 3 H, CH₃ keto), 2.15 (s, 3 H, CH₃ enol), 6.8 (m, 1 H, Ar), 6.9 (d, 1 H, Ar), 7.03 (d, 1 H, Ar), 8.26 (s, 1 H, CH keto), 8.23 (s, 1H, CH enol) 11.1 (s, 1 H, Ar OH), 11.2 (s, 1 H, Ar OH), 11.6 (s, 1 H, NH keto), 9.1 (s, 1 H, OH enol) ppm. ¹³C NMR ([D₆]DMSO): δ = 21.0 (CH₃ keto), 22.0 (CH₃ enol), 166.1 (C=O keto), 172.1 (C–OH enol), 142.5 (CH keto), 147.7 (CH enol), 117.2, 117.8, 119.7, 120.7, 145.8, 146.2 (Ar keto); 119.3, 118.8, 119.9, 120.9, 146.2, 146.6 (Ar enol) ppm.

[Mn(HL¹)₂][ClO₄]₂·2H₂O (1): Mn(ClO₄)₂·xH₂O (0.379 g, 1.5 mmol) was dissolved in an acetonitrile/methanol (1:1, 10 mL) mixture, and solid HL¹ (0.045 g, 0.25 mmol) was added. The mixture was heated under reflux at 80 °C for 1 h. The light yellow solution was kept at room temperature (ca. 30 °C) for slow evaporation. Light yellow plate-shaped single crystals suitable for X-ray diffraction were obtained after two weeks and were accompanied by a small amount of octahedral single crystals, yield 0.400 g (ca. 62%). FTIR (KBr): $\tilde{v} = 1548 [v(C=N)]$, 1605 [v(C=O)], 3076 [v(N-H)], 432 [v(Mn-N)] cm⁻¹. UV/Vis: $\lambda_{max} = 287 (\pi \rightarrow \pi^*)$, 318 (n $\rightarrow \pi^*$), 365 (LMCT) nm.

{[Mn(HL¹)₂]·[Mn(L¹)₂]}[ClO₄]₂ (2): Mn(ClO₄)₂·xH₂O (0.379 g, 1.5 mmol) was dissolved in an acetonitrile/methanol mixture (10 mL), and solid HL¹ (0.045 g, 0.25 mmol) was added. The mixture was stirred for 0.5 h at room temperature (ca. 30 °C). The light yellow solution was kept at room temperature for slow evaporation. Light yellow single crystals suitable for X-ray diffraction were obtained after two weeks, yield 0.795 g (78%). FTIR (KBr): $\tilde{v} = 1559$ [v(C=N)], 1596 [v(C=O)], 2851 [v(N-H)], 415 [v(Mn-N)] cm⁻¹. UV/Vis: $\lambda_{max} = 289 (\pi \rightarrow \pi^*)$, 322 (n $\rightarrow \pi^*$), 366 (LMCT) nm.

 $[Mn(\mu-HL^2)(H_2O)]_2[ClO_4]_2$ (3): $Mn(ClO_4)_2 \cdot xH_2O$ (0.379 g, 1.5 mmol) was dissolved in an acetonitrile/2-propanol mixture (1:1, 10 mL), and solid H_2L^2 (0.25 mmol, 0.05 g) was added. The mixture was allowed to stir for 0.5 h with heating at 60 °C. The light yellow solution was kept at room temperature for slow evaporation (ca. 30 °C). Light yellow prismatic single crystals suitable for X-

Table 4. Crystal structure parameters.

	HL ¹	H_2L^2	1	2	3
Formula	$C_9H_{10}N_2O_2$	$C_9H_{10}N_2O_3$	C ₁₈ H ₂₄ Cl ₂ Mn ₁ N ₄ O ₁₄	C ₃₆ H ₃₈ Cl ₂ Mn ₂ N ₈ O ₁₆	$C_9H_{13}Cl_1Mn_1N_2O_9$
Formula weight	178.19	194.19	646.24	1019.50	383.59
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P12_1/n$	PĪ	$P2_1/c$	PĪ
a /Å	4.50(3)	6.07(4)	9.71(6)	12.95(8)	8.18(4)
b /Å	26.24(4)	11.52(1)	12.08(8)	24.88(9)	9.11(6)
c /Å	7.50(4)	13.11(1)	13.15(7)	15.06(1)	10.82(7)
a /°	90	90	112.74(6)	90	92.53(5)
β /°	95.38(9)	94.36(5)	99.27(5)	114.72(5)	112.07(5)
y /°	90	90	105.65(6)	90	98.07(5)
$V/Å^3$	881.6(1)	913.5(9)	4522(3)	4408(2)	735.62(8)
Ζ	4	4	2	4	2
$D/\text{g}\text{cm}^{-3}$	1.342	1.41	1.642	1.54	1.732
μ /mm ⁻¹	0.097	1.08	0.785	7.72	1.126
F (000)	376	408	662	2088	390
Crystal size /mm	$0.05 \times 0.13 \times 0.47$	$0.09 \times 0.12 \times 0.29$	$0.14 \times 0.24 \times 0.29$	$0.16 \times 0.24 \times 0.30$	$0.12 \times 0.14 \times 0.45$
θ range /°	2.8-29.2	3.1-29.19	2.9-29.2	2.9-29.21	2.9-29.2
Refl. collected	3923	4618	10986	16506	6135
Independent refl.	1903	2136	6000	9001	3392
R(int)	0.067	0.033	0.031	0.029	0.025
Refl. used	601	1157	4279	5977	2173
Parameters refined	118	127	352	604	199
S	1.1	1.1826	1.1040	1.0668	1.02
Final R indices	R = 0.0475	R = 0.0410	R = 0.0487	R = 0.0804	R = 0.0552
	$wR = 0.0562 [I > 3\sigma(I)]$	$wR = 0.0384 [I > 0\sigma(I)]$	$wR = 0.0657 [I > 0\sigma(I)]$	$wR = 0.0845 [I > 2\sigma(I)]$	$wR = 0.0836 [I > 3\sigma(I)]$
Residuals /e Å ⁻³	0.16, -0.21	0.18, -0.18	0.60, -0.40	1.31, -0.92	0.93, -0.63



ray diffraction were obtained after one month. The crystals were collected by filtration and air-dried before X-ray diffraction, yield 0.296 g (76%). FTIR (KBr): $\tilde{v} = 1567 [v(C=N)]$, 1615 [v(C=O)], 2858 [v(N-H)], 421 [v(Mn-N)] cm⁻¹. UV/Vis: $\lambda_{max} = 310 (\pi \rightarrow \pi^*)$, 356 ($n \rightarrow \pi^*$), 385 (LMCT) nm.

X-ray Crystallography: The X-ray diffraction data of all the compounds were collected with an Oxford Diffraction Gemini Diffractometer^[29] containing an area detector and a graphite monochromator with Mo- K_{α} radiation ($\lambda = 0.71069$ Å). Data collection and reduction were performed with the CrysAlis program.^[30] The structures were solved by direct methods with the program SIR92^[31] followed by Superflip^[32] and refined with the program CRYSTALS.^[33] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on *F*. All other H atoms were generated geometrically and included in the refinement in a riding model approximation. Experimental absorption correction was performed by an analytical technique. The crystallographic data for the ligands and **1–3** are summarized in Table 4.

CCDC-1014123 (for HL¹), -1014124 (for H₂L²), -1014125 (for 1), -1014126 (for 2) and -1014127 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): PXRD patterns of 1–3, ¹H and ¹³C NMR assignment schemes for HL¹ and H₂L², ¹H and ¹³C NMR spectra of HL¹ and H₂L², FTIR spectra of the ligands and complexes.

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