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CD spectroscopy as a fingerprint technique for the structural characterization and determination of absolute configurations of unsymmetric chiral Schiff base Ni(II) complexes

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ABSTRACT

Unsymmetric Schiff base complexes have attracted more attention in recent years due to their diverse effects in catalytic reactions. Due to their high dissymmetry, unsymmetric metallosalen complexes are harder to prepare than symmetric ones. This means that X-ray crystallographic structural determination is sometimes unavailable, so their absolute configurations are determined by circular dichroism (CD) spectroscopy instead. Herein, some quadridentate unsymmetric metallosalen nickel(II) complexes were synthesized and their structures were characterized by CD spectra. An empirical rule for assignment of the absolute configurations of tetra-coordinated pseudo-planar Ni(II) complexes was put forward. Furthermore, a fingerprint was found to judge whether the metallosalen complexes are symmetric or unsymmetric.

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1. Introduction

Schiff base metal complexes are known to be biologically important,¹ and have been shown to be highly effective catalysts in various chemical and photochemical reactions such as the enantioselective epoxidation of unfunctionalized olefins by chiral Mn(III) Schiff base complexes.^{1a–d} Chiral C_2 -symmetric metallosalen complexes, derived from the condensation of optically active 1,2-diamines with 2 equiv of substituted salicylaldehydes (SAL) or dehydroacetic acids (DHA), have been successfully used in asymmetric catalytic epoxidations.^{1d–f}

Most of the reported chiral metallosalen complexes are C_2 -symmetric.^{2a,b} However, in recent years, chiral unsymmetric metallosalen complexes have attracted more attention. By optimizing the structure, it is possible to obtain chiral environments inaccessible for C_2 symmetric complexes. Due to their higher dissymmetry, unsymmetric metallosalen complexes have shown diverse effects in catalyzed reactions and sometimes enhance the catalytic effectiveness.^{2c-e} Unfortunately, these are much more difficult to prepare than those of the symmetric ones, as it is harder to obtain their crystal structures. In addition, the condensations resulting in unsymmetric metallosalen complexes may sometimes rearrange to the corresponding symmetric ones in the presence of metal

ions.^{2f} Thus, the synthetic unsymmetric metallosalen complexes may often be contaminated by the symmetric ones. Small changes in their structures generally lead to a remarkable change in catalytic effectiveness; it is necessary to find a convenient method to distinguish between unsymmetric and symmetric metallosalen complexes in situ. In addition, X-ray crystallographic structural determination is frequently unavailable in this case. As a result, it is important to determine their absolute configuration by other method such as CD spectroscopy.

The assignment of the absolute configurations of the molecules requires the knowledge of the molecular structure and an observable signal that can be assigned to one of the two enantiomers. Xray crystallographic structural determination is the first available method of this sort. Several chiroptical spectroscopic techniques, such as nonempirical exciton coupled circular dichroism (ECCD), have been used to assign the absolute configurations of molecules when their structures have been known.^{3a,b} For the chiral quadridentate metallosalen complexes, CD spectroscopy is useful in determining their absolute configuration by comparing the CD spectra in the UV region with similar molecules; their absolute configurations have been determined by X-ray crystallographic structural determination or ECCD.^{3c-h} These results are in accordance with predictions of the exciton chirality method.^{3b,i,j} However, because the bands corresponding to the dipole-dipole interactions between more than two chromophores may overlap with one another, confirming the CD splitting pattern in the UV regions is sometimes difficult. Thus, some empirical correlations between the CD pattern in other regions and the absolute configuration for such chiral metal complexes have been reported.^{3k}

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Herein, two series of nickel(II) complexes (Fig. 1) with unsymmetric quadridentate Schiff bases prepared from the condensation of 2-hydroxyacetophenone (HACP), DHA, BuSAL, and bromosalicylaldehyde (BrSAL) with optically active *trans*-cyclohexane-1,2-diamine (chxn), 1,2-diphenyl-ethylenediamine (dpen) were synthesized and characterized by EA, IR, UV–vis, and CD spectra. The absolute configurations of these complexes were assigned by their CD spectra. An empirical rule was worked out to determine the absolute configurations of both symmetric and unsymmetric pseudo-planar Ni(II) metallosalen complexes. A fingerprint was found to judge whether the metallosalen complexes are symmetric or unsymmetric.

2. Results and discussion

Enantiomerically pure 1,2-diphenylethylenediamine (dpen) is commercially available. Diastereomeric *trans*-cyclo-hexane-1,2diamine tartrates were prepared by the reported methods.^{1d,4} The chiral diamines were set free from the corresponding tartrates and were used in situ according to the method that was previously reported by us.⁴ The free chiral diamines were dissolved in methanol, mixed with 1 equiv. of DHA in dichloromethane solution in the presence of MgSO₄ and stirred at room temperature for 10 h.^{1f} The yellow solution was filtered, evaporated to dryness, and recrystallized from dichloromethane/methanol (1:1). The resulting yellow product was dissolved in ethanol, mixed with 1 equiv of HACP or BrSAL in ethanol, and stirred at reflux for 8 h. The yellow solution was evaporated, recrystallized from dichloromethane/methanol (1:1), and dried in vacuum at room temperature.

An appropriate amount of chiral Schiff base dissolved in methanol was allowed to reflux under an inert atmosphere with $Ni(OAc)_2$ ·4H₂O (1 equiv) in the presence of triethylamine (1 equiv) for 30 min (Scheme 1).^{1f} The solution was filtered and concentrated to dryness. The resulting residue was washed in ethanol, recrystallized from dichloromethane, and dried in vacuum. The overall yields for the complexes were in the range of 68–78%.

In the UV–vis spectra of unsymmetric Schiff bases, the azomethine π – π^* transition bands lie at 317–328 nm (ε = 3500–18,000) and the benzene π – π^* transition bands lie at 220–233 nm (ε = 30,000–45,000). The UV–vis spectra of each complex are shown in Figure 2. Compared with the spectra of Schiff bases, the azomethine π – π^* transition bands lie at about 315 nm (ε = 8000–18,000). The benzene π – π^* transition bands red shift to 230–250 nm (ε = 30,000–45,000). The d–d transition bands are not observed due to the low concentration, ~10⁻⁴ to 10⁻⁵ mol/L of the complex solution. There should be low-intensity bands at about 550 nm according to their CD spectra.

The CD spectra of the Schiff bases are approximately mirror images of those of their respective enantiomers. The complexes prepared from a Schiff base and its enantiomers give a symmetric CD pattern (Fig. 3). These results reveal that a chiral unsymmetric Schiff base will induce a stereoselective synthesis of the corresponding complex with specific stereochemistry.

According to the respective UV–vis spectrum, the bands at about 230 nm are assigned to the benzene π – π ^{*} transitions. The bands at about 310 nm are the azomethine π – π ^{*} transitions. The weak bands at 380 nm and 415 nm are considered to be the LMCT transitions.^{3g,h,5} The d–d transition bands at 540–560 nm show a weak Cotton effect (CE), and can be interpreted as the ${}^{1}A_{1}(F) \rightarrow {}^{1}B_{1}$ transition.^{3m}

Comparing the CD spectra of the complexes with relevant Schiff bases, the bands observed in the Schiff bases are still observed in the relevant complexes, but have shifted more or less. Because of the distortion of the chelate ring, the two azomethine π - π ^{*} transitions interact with each other and cause an exciton pattern couplet around 320 nm (Fig. 3a).

The CD spectra of the complexes prepared from different chiral diamine show distinct difference. In the CD spectra of DHA–(*SS*)(*RR*)dpen–BrSAL–Ni, the strong band that lies near 310 nm can be assigned to the absorbance of the benzenes on 1,2-diphen-ylethylenediamine itself. The stereoeffect of the two benzenes causes the pseudo-planar coordination environment around the metal center in the DHA–(*SS*)(*RR*)dpen–BrSAL–Ni to contort less than in the DHA–(*SS*)(*RR*)chxn–BrSAL–Ni.^{3e} Thus, the intensity of the CD band in the d–d region for DHA–(*SS*)(*RR*)dpen–BrSAL–Ni ($\Delta \varepsilon_{545} = 0.95/-0.92 \text{ L mol}^{-1} \text{ cm}^{-1}$) is lower than for DHA–(*SS*)(*RR*)chxn–BrSAL–Ni ($\Delta \varepsilon_{560} = -4.80/4.36 \text{ L mol}^{-1} \text{ cm}^{-1}$). Similar situation is also observed in the corresponding symmetric metal-losalen complexes.

When comparing the CD spectra of the unsymmetric metallosalen complexes with the symmetric ones, the locations of the main bands are similar. However, more exciton couplets are observed in the UV region of the unsymmetric complexes. This can be attributed to the fact that the lower symmetry causes the degenerate energy levels of the transitions to split. Furthermore, a new band, weak but remarkable, can be observed in the CD spectra of the unsymmetric metallosalen complexes at about 460–480 nm. It is not found in the corresponding region of the CD spectra of any symmetric complexes. The existence of this fingerprint may be attributed to the splitting of the energy levels of the d-d transitions of the metal located in the coordination environment with lower symmetry. By examining whether this fingerprint appears in the CD spectra or not, it is quite easy to distinguish between most of the symmetric metallosalen complexes and the unsymmetric ones.

The absolute configurations of the metallosalen complexes prepared from salicylaldehyde and chiral diamine [(S)-1,2-pn, (S)-1,2-bn, (S)-1,2-dpen, (S)-trans-1,2-chxn, etc.] have been determined by Pasini using the exciton chirality method.^{3e} However, for some complexes, such as those prepared from DHA, confirming the CD splitting pattern in the UV region is sometimes diffi-



HACP: $R^2 = CH_3$, $R^3 = H$ BrSAL: $R^2 = H$, $R^3 = BrBuSAL$: $R^2 = H$, $R^3 = t$ -Bu

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Figure 1. Unsymmetric metallosalen complexes.



Scheme 1. Synthesis of unsymmetric metallosalen complexes.



Figure 2. UV-vis spectra of unsymmetric metallosalen.

cult because the bands that correspond to the dipole-dipole interactions between more than two chromophores may overlap with one another. A distinctive band of d-d transition can be observed at 500-600 nm in the CD spectra of the tetra-coordinated pseudo-planar metallosalen complexes. Its CE sign is dependent on the absolute configuration. We have put forward an empirical rule to determine the absolute configuration of the symmetric nickel(II) metallosalen complexes in the past. In the case of tetra-coordinated pseudo-planar Ni(II) symmetric complexes, the following empirical rule exists: (i) $(S)\Delta\lambda$ for the HACP–(S)-pn, HACP-(SS)-dpen, DHA-(S)-pn, DHA-(SS)-dpen derivatives, which is reflected by the positive CE around 550 nm; and (ii) (S) $\Lambda\delta$ for the HACP-(SS)-chxn, DHA-(SS)-chxn derivatives with a concomitant inversion of the CE.^{3k} In the symmetric and unsymmetric metallosalen complex series, the stereostructures and coordination environments are all quite similar. Thus, this empirical rule may also be applicable for unsymmetric metallosalen complexes (Table 1). For DHA-(SS)-dpen-BrSAL-Ni, DHA-(SS)-dpen-HACP-Ni, DHA-(SS)-dpen-Bu-SAL-Ni, the sign of the CD pattern around 550 nm is positive. This implies that the chirality is $\Delta \lambda$ where lowercase symbols reflect the chirality (or conformation) of the ethylenediamine chelate ring and the uppercase symbols reflect that of the tetrahedral distortion of the metal coordination. For DHA-(RR)-dpen-BrSAL-Ni, DHA-(RR)-dpen-HACP-Ni, DHA-(RR)dpen-Bu-SAL-Ni, the sign is negative, which imply the chirality $\Lambda\delta$. For DHA-(SS)(RR)-chxn-BrSAL-Ni, DHA-(SS)(RR)-chxn-HACP-Ni, DHA-(SS)(RR)-chxn-Bu-SAL-Ni, the relationship between the chiral diamine and the absolute configuration of the complexes derived from it is the inverse. The reason for this exception is that the presence of the two fused rings forces the molecule to distort to the most stable configuration with an inverse chirality compared with the corresponding complexes derived from other chiral diamine.

Herein, the exciton chirality method is used to validate the above-mentioned results. For an exciton couplet pattern, the CD sign of the band of higher energy is determined by the sign of the product of the rotational strength (\mathbf{R}) and the dipole interaction energy (V_{12}), where **R** and V_{12} are given by Eqs. 1 and 2. In fact, only the angular dependent part of Eqs. 1 and 2 is necessary for determining the sign of the CD signal.³¹ For $(HACP)_2 - (RR)$ chxn–Ni, whose absolute configuration has been assigned to $\Delta \lambda$ by X-ray crystallographic structural determination, angle γ for the exciton splitting of the azomethine $\pi - \pi^*$ transition is obtained from its crystal structure data, $^{3k,o} \alpha$ and β can be estimated, 3n and the sign of $\mathbf{R} \cdot \mathbf{V}_{12}$ is positive according to the Eqs. 1 and 2. This means that the CD sign of the band in longer wavelength of the exciton couplet pattern of (HACP)2-(RR)-chxn-Ni around 320 nm should be negative. However, the exciton couplet pattern cannot be observed in this range because the bands of the chromophores in the molecule overlap with one another. On the basis of the exciton chirality method, the substitution of a ligand with retention of configuration in the case of degenerate coupling with a similar chromophore does not change the CD spectra qualitatively.³¹ Thus, the DHA-(RR)-chxn-BrSAL-Ni should have an exciton couplet pattern around 320 nm with negative chirality, whose absolute configuration has been assigned to $\Delta \lambda$ above. This is consistent with the experimental CD spectra (Fig. 3a). On the other hand, unlike in the Zn(II) and Cu(II) metallosalens,^{3d,p} the charge transfer transitions in Ni(II) metallosalens may overlap their exciton split bands sometimes.^{3d} Hence, in most cases, it is difficult to observe the exciton couplet pattern clearly (Fig. 3b-f).

$$\mathbf{V}_{12} = \frac{1}{4\pi\varepsilon_0} \frac{\mu^2}{r_{12}^3} (\sin\alpha\sin\beta\cos\gamma + 2\cos\alpha\cos\beta) \tag{1}$$

$$\mathbf{R}^{\pm} = \pm 0.5\pi \tilde{\nu} m^2 \sin \alpha \sin \beta \sin \gamma \tag{2}$$

In addition, the solid-state CD spectra of all the unsymmetric complexes mentioned above were studied. The results, similar to those of symmetric metallosalens,⁶ revealed that all chiral com-



Figure 3. CD spectra of complexes DHA-chxn-BrSAL-Ni(II) (a), DHA-chxn-BuSAL-Ni(II) (b), DHA-chxn-HACP-Ni(II) (c), DHA-dpen-BrSAL-Ni(II) (d), DHA-dpen-BuSAL-Ni(II) (e), DHA-dpen-HACP-Ni(II) (f), Red is (SS), blue is (RR).

 Table 1

 Absolute configuration of the complexes and corresponding CD sign in the 500–600 nm range

	Absolute configuration	CD sign
Symmetric complex ^{3k}		
(HACP) ₂ -(SS)-dpen-Ni	Δ	+
(HACP) ₂ -(<i>RR</i>)-dpen-Ni	Λ	_
(HACP) ₂ –(SS)-chxn–Ni	Λ	-
(HACP) ₂ –(<i>RR</i>)-chxn–Ni	Δ	+
(DHA) ₂ –(SS)-dpen–Ni	Δ	+
(DHA) ₂ –(<i>RR</i>)-dpen–Ni	Λ	_
(DHA) ₂ -(SS)-chxn-Ni	Λ	_
(DHA) ₂ -(<i>RR</i>)-chxn-Ni	Δ	+
Unsymmetric complex		
DHA–(SS)-dpen–BrSAL–Ni	Δ	+
DHA-(RR)-dpen-BrSAL-Ni	Λ	-
DHA–(SS)-dpen–HACP–Ni	Δ	+
DHA–(RR)-dpen–HACP–Ni	Λ	-
DHA-(SS)-dpen-BuSAL-Ni	Δ	+
DHA-(RR)-dpen-BuSAL-Ni	Λ	_
DHA–(SS)-chxn–BrSAL–Ni	Λ	_
DHA–(RR)-chxn–BrSAL–Ni	Δ	+
DHA–(SS)-chxn–HACP–Ni	Λ	-
DHA–(RR)-chxn–HACP–Ni	Δ	+
DHA–(SS)-chxn–BuSAL–Ni	Λ	-
DHA–(RR)-chxn–BuSAL–Ni	Δ	+

plexes maintain the same configurations found in solution states. Furthermore, the solid-state CD spectra are sometimes more sensitive.

3. Conclusion

In conclusion, by comparison of the CD spectra of the unsymmetric complexes, the CD signal in the d-d transition region is useful as a reference in determining the chiral configurations of the complexes. In the case of tetra-coordinated pseudo-planar Ni(II) complexes, we therefore have the following empirical rule: (i) for both symmetric and unsymmetric complexes prepared from any chiral diamine, the positive Cotton effects around 550 nm reveal the $\Delta\lambda$ chirality, and vice versa; (ii) for both symmetric and unsymmetric complexes prepared from dpen, the $\Delta\lambda$ chirality corresponds to the (SS)-configuration of the chiral diamine, and vice versa; (iii) for both symmetric and unsymmetric complexes prepared from chxn, the $\Delta \lambda$ chirality corresponds to the (*RR*)-configuration of the chiral diamine, and vice versa. This can be used to assign the absolute configuration of some tetrahedral or pseudoplanar metallosalen complexes with similar electronic configurations and coordination spheres. Moreover, it may meet the need for in situ assignment of absolute configurations and conformations of some chiral diamines by the CD spectra of their metallosalen complexes. In addition, the existence of the CD fingerprint at 460–480 nm means that the complex is unsymmetric, and vice versa. This can also lead to an easy method to judge whether the metallosalen complexes are symmetric or unsymmetric. Further studies are under investigation.

4. Experimental

4.1. General

Unless otherwise noted, all starting materials and solvents were obtained from commercial suppliers and used without further purification. Infrared spectra (KBr pellets) were recorded on a Nicolet 360 FT-IR spectrometer in the range of 400–4000 cm⁻¹. UV–vis and CD spectra were performed, respectively, on a Shimadzu UV-2501 PC spectrophotometer and a JASCO J-810 spectropolarimeter. Elemental analysis was obtained from an Elementar Vario EL III elemental analyzer. ¹H NMR spectra were measured on a Bruker DRX400 NMR spectrometer in CDCl₃ using tetramethylsilane as the internal standard. The UV–vis and CD spectra were obtained at room temperature with the same methanol solutions ranging from 10^{-4} to 10^{-5} mol/L using 5 mm quartz cells.

4.2. *N*-(1*S*,2*S*)-1,2-Cyclohexylene(5-bromo-2-hydroxyformylphenonylideneiminato)-*N*'-{(4-hydroxy-6-methyl-2-pyrone)3acetylidine} nickel(II)

A brick red solid, 73%, mp >300 °C. IR(KBr): v 2934 (–CH₂CH₃), 1621 (C=N), 1183 (C–N), 1322 (C–O), 582 (Ni–N), 448 (Ni–O) cm⁻¹. ¹H NMR (CDCl₃, TMS, 400 MHz, ppm): 1.26 (2H, m, CH₂), 1.70 (4H, m, 2×CH₂), 1.90 (2H, m, CH₂), 2.08 (3H, s, CH₃), 2.57 (3H, s, CH₃), 3.01 (H, m, CH–N), 3.58 (1H, m, CH–N), 5.87 (H, s, CH), 6.79–7.25 (3H, m, Ar), 7.26 (H, s, CH). Anal. Calcd for C₂₁H₂₁N₂O₄BrNi: requires: C, 50.04; H, 4.20; N, 5.56. Found: C, 50.32; H, 4.43; N, 5.18.

4.3. *N*-(1*R*,2*R*)-1,2-Cyclohexylene(5-bromo-2-hydroxyformylphenonylideneiminato)-*N*'-{(4-hydroxy-6-methyl-2-pyrone)3acetylidine} nickel(II)

A brick red solid, 76%, mp >300 °C. IR(KBr): v 2934 (–CH₂CH₃), 1621 (C=N), 1183 (C–N), 1322 (C–O), 582 (Ni–N), 448 (Ni–O) cm⁻¹. Anal. Calcd for C₂₁H₂₁N₂O₄BrNi: requires: C, 50.04; H, 4.20; N, 5.56. Found: C, 50.35; H, 4.45; N, 5.16.

4.4. *N*-(1*S*,2*S*)-1,2-Diphenylethylene(5-bromo-2-hydroxyformyl phenonylideneiminato)-*N*-{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} nickel(II)

A brick red solid, 75%, mp >300 °C. IR(KBr): v 2924 (-CH₂CH₃), 1618 (C=N), 1179 (C-N), 1320 (C-O), 549 (Ni–N), 466 (Ni–O) cm⁻¹. ¹H NMR (CDCl₃, TMS, 400 MHz, ppm): 2.15 (3H, s, CH₃), 2.23 (3H,s, CH₃), 4.40 (H, m, CH–N), 4.66 (1H, m, CH–N), 6.04 (H, m, CH), 6.93–7.59 (10H, m, 2Ph), 7.98–7.99 (2H, m, Ar), 8.44– 8.45(2H, m, Ar, CH). Anal. Calcd for C₂₉H₂₃N₂O₄BrNi: requires: C, 57.85; H, 3.85; N, 4.65. Found: C, 57.68; H, 3.66; N, 4.74.

4.5. *N*-(1*R*,2*R*)-1,2-Diphenylethylene(5-bromo-2-hydroxyformyl phenonylideneiminato)-*N*-{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} nickel(II)

A brick red solid, 75%, mp >300 °C. IR(KBr): v 2924 (–CH₂CH₃), 1618 (C=N), 1179 (C–N), 1320 (C–O), 549 (Ni–N), 466 (Ni–O) cm⁻¹. Anal. Calcd for C₂₉H₂₃N₂O₄BrNi: requires: C, 57.85; H, 3.85; N, 4.65. Found: C, 57.63; H, 3.46; N, 4.88.

4.6. *N*-(1*S*,2*S*)-1,2-Diphenylethylene(5-tertbutyl-2-hydroxyformylphenonylideneiminato)-*N*'-{(4-hydroxy-6-methyl-2pyrone)3-acetylidine} nickel(II)

A brick red solid, 76%, mp > 300 °C. IR(KBr): v 2926 (–CH₂CH₃), 1613 (C=N), 1174 (C–N), 1332 (C–O), 548 (Ni–N), 474 (Ni–O) cm⁻¹. Anal. Calcd for C₃₃H₃₂N₂O₄Ni: requires: C, 68.42; H, 5.57; N, 4.84. Found: C, 68.23; H, 5.70; N, 4.39.

4.7. N-(1R,2R)-1,2-Diphenylethylene(5-tertbutyl-2-hydrox yformylphenonylideneiminato)-N'-{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} nickel(II)

A brick red solid, 79%, mp >300 °C. IR(KBr): v 2926 (–CH₂CH₃), 1613 (C=N), 1174 (C–N), 1332 (C–O), 548 (Ni–N), 474 (Ni–O) cm⁻¹. Anal. Calcd for C₃₃H₃₂N₂O₄Ni: requires: C, 68.42; H, 5.57; N, 4.84. Found: C, 68.88; H, 5.32; N, 5.01.

4.8. *N*-(1*S*,2*S*)-1,2-Diphenylethylene(2-hydroxyacetophenonylideneiminato)-*N*'-{(4-hydroxy-6-methyl-2pyrone)3-acetylidine} nickel(II)

A brick red solid, 78%, mp >300 °C. IR(KBr): v 2924 (–CH₂CH₃), 1615 (C=N), 1173 (C–N), 1318 (C–O), 547 (Ni–N), 468 (Ni–O) cm⁻¹. ¹H NMR (CDCl₃, TMS, 400 MHz, ppm): 2.07 (3H, s, CH₃), 2.10 (3H, s, CH₃), 2.14 (3H, s, CH₃), 4.61 (H, m, CH–N), 4.74 (1H, m, CH–N), 5.93 (H, m, CH), 7.02–7.79 (14H, m, Ar). Anal. Calcd for C₃₀H₂₆N₂O₄Ni: requires: C, 67.07; H, 4.88; N, 5.21. Found: C, 67.22; H, 5.22; N, 5.02.

4.9. *N*-(1*R*,2*R*)-1,2-Diphenylethylene(2-hydroxyacetophenonylideneiminato)-*N*'-{(4-hydroxy-6-methyl-2-pyrone)3acetylidine} nickel(II)

A brick red solid, 78%, mp >300 °C. IR(KBr): v 2924 (–CH₂CH₃), 1615 (C=N), 1173 (C–N), 1318 (C–O), 547 (Ni–N), 468 (Ni–O) cm⁻¹. Anal. Calcd for C₃₀H₂₆N₂O₄Ni: requires: C, 67.07; H, 4.88; N, 5.21. Found: C, 67.46; H, 4.97; N, 5.34.

4.10. *N*-(1*S*,2*S*)-1,2-Cyclohexylene(2-hydroxyacetophenonylideneiminato)-*N*'-{(4-hydroxy-6-methyl-2-pyrone)3acetylidine} nickel(II)

A brick red solid, 71%, mp >300 °C. IR(KBr): v 2927 (-CH₂CH₃), 1622 (C=N), 1180 (C-N), 1325 (C-O), 583 (Ni–N), 452 (Ni–O) cm⁻¹. ¹H NMR (CDCl₃, TMS, 400 MHz, ppm): 1.36 (2H, m, CH₂), 1.66 (4H, m, 2×CH₂), 1.83 (2H, m, CH₂), 2.08 (3H, s, CH₃), 2.46 (3H, s, CH₃), 2.52 (3H, s, CH₃), 3.71 (H, m, CH–N), 3.98 (1H, m, CH–N), 5.84 (H, s, CH), 6.85–7.47 (4H, m, Ar). Anal. Calcd for C₂₂H₂₄N₂O₄Ni: requires: C, 60.17; H, 5.51; N, 6.38. Found: C, 59.98; H, 6.66; N, 6.44.

4.11. *N*-(1*R*,2*R*)-1,2-Cyclohexylene(2-hydroxyacetophenonylideneiminato)-*N*'-{(4-hydroxy-6-methyl-2pyrone)3-acetylidine} nickel(II)

A brick red solid, 73%, mp >300 °C. IR(KBr): v 2927 (–CH₂CH₃), 1622 (C=N), 1180 (C–N), 1325 (C–O), 583 (Ni–N), 452 (Ni–O) cm⁻¹. Anal. Calcd for C₂₂H₂₄N₂O₄Ni: requires: C, 60.17; H, 5.51; N, 6.38. Found: C, 59.89; H, 6.61; N, 6.74.

4.12. *N*-(1*S*,2*S*)-1,2-Cyclohexylene(5-tertbutyl-2hydroxyformylphen onylideneiminato)-*N*-{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} nickel(II)

A brick red solid, 69%, mp >300 °C. IR(KBr): v 2924 (-CH₂CH₃), 1619 (C=N), 1182 (C-N), 1327 (C-O), 578 (Ni-N), 447 (Ni-O) cm^{-1.} ¹H NMR (CDCl₃, TMS, 400 MHz, ppm): 1.26 (9H, s, $3 \times CH_3$), 1.33 (2H, m, CH₂), 1.67 (4H, m, $2 \times CH_2$), 1.80 (2H, m, CH₂), 2.08 (3H, s, CH₃), 2.54 (3H, s, CH₃), 2.97 (H, m, CH–N), 3.53 (1H, m, CH–N), 5.87 (H, s, CH), 6.86–7.17 (3H, m, Ar), 7.27 (H, s, CH). Anal. Calcd for C₂₅H₃₀N₂O₄Ni: requires: C, 62.40; H, 6.28; N, 5.82. Found: C, 61.87; H, 6.36; N, 6.01.

4.13. *N*-(1*R*,2*R*)-1,2-Diphenylethylene(5-tertbutyl-2-hydroxy-formylphenonylideneiminato)-*N*'-{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} nickel(II)

A brick red solid, 74%, mp >300 °C. IR(KBr): v 2924 (–CH₂CH₃), 1619 (C=N), 1182 (C–N), 1327 (C–O), 578 (Ni–N), 447 (Ni–O) cm⁻¹. Anal. Calcd for C₂₅H₃₀N₂O₄Ni: requires: C, 62.40; H, 6.28; N, 5.82. Found: C, 62.15; H, 5.97; N, 5.78.

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