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Synthesis and characterization of chiral nickel(II) Schiff base complexes and their CD spectra-absolute configuration correlations

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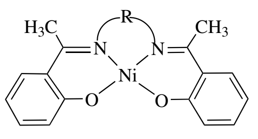
Abstract—Some nickel(II) complexes of quadridentate Schiff bases prepared from the condensation of 2 mol of 2-hydroxyacetophenone (HACP) or dehydroacetic acid (DHA) with 1 mol of optically active propylene-1,2-diamine (pn), *trans*-cyclohexane-1,2-diamine (chxn) or 1,2-diphenylethylenediamine (dpen) were synthesized and characterized by EA, IR, UV–vis, and CD spectra. The absolute configurations of the three complexes were determined by X-ray single crystal structure measurement and correlated with CD spectroscopy. In this study, special attention is focussed on the CD signals of the related complexes in the d–d transition region, in the hope of obtaining a tentative correlation between the CD pattern and the absolute configuration about the central metal. A new empirical rule for the assignment of the absolute configuration around the nickel ion in each complex and the handedness of the chiral diamine contained in the Schiff base ligand is put forward. In the case of tetra-coordinated pseudo-planar Ni(II) complexes, the rule can be stated as follows: (i) a positive Cotton effect in the d–d region around 550 nm is assigned to the (S)$\Delta\lambda$-configuration for the HACP-(S)-pn-Ni, HACP-(SS)-dpen-Ni, DHA-S-pn-Ni, and DHA-(SS)-dpen-Ni derivatives; and (ii) a concomitant inversion of the Cotton effect in the same range is assigned to the (S)$\Lambda\delta$-configuration for the HACP-(SS)-chxn-Ni and DHA-(SS)-chxn-Ni derivatives.

1. Introduction

Metallic complexes of Schiff bases are known to be biologically important and serve as catalysts in various chemical and photochemical reactions.[1] The major advances in the enantioselective epoxidation of unfunctionalized olefins have been achieved with chiral Mn(III) Schiff base complexes, which were reported by Jacobsen's and Katsuki's groups independently.[1,2] Chiral Schiff base complexes derived from the condensation of optically active 1,2-diamines with 2 equiv of substituted salicylaldehydes (SAL) or dehydroacetic acids (DHA) have been used successfully in the asymmetric catalytic epoxidation.[2,3] It has been known that circular dichroism (CD) spectra are relevant for the characterization of chiral quadridentate sal-diamine complexes because they provide insights into conformations of the complexes as well as the assignments of their absolute configurations based on the comparison between the CD spectra of the complexes containing different sal-diamines in the UV region.[4,5] These results agree with the predictions of the exciton chirality method.[6] However, rarely have the conformational trends in the other class of the chiral Schiff base complexes been discussed in the literature. It is noteworthy that sometimes the CD splitting patterns in the UV region are difficult to confirm because the bands corresponding to the dipole–dipole interactions between more than two chromophores can overlap each other. Therefore, it is necessary to find another empirical correlation between the CD patterns and the absolute configuration for such chiral metal complexes.



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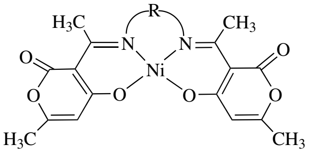

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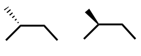
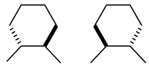
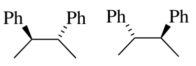


a. 1,2-pn



b. *trans*-1,2-chxn



c. 1,2-dpen

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Herein, two series of nickel(II) complexes with quadridentate Schiff bases prepared from the condensation of 2-hydroxyacetophenone (HACP) or DHA with optically active propylene-1,2-diamine (pn), *trans*-cyclohexane-1,2-diamine (chxn), 1,2-diphenylethylenediamine (dpen) were synthesized and characterized by EA, IR, UV–vis, and CD spectra. The absolute configurations of the complexes were correlated with X-ray single crystal structure measurement and CD spectroscopy. Special focus is on the CD bands in the d–d transition region. We carried out this study in order to determine the absolute configurations of pseudo-planar Ni(II) Schiff base complexes with a new empirical rule.

2. Results and discussion

Diastereomeric propylene-1,2-diamine tartrates and *trans*-cyclohexane-1,2-diamine tartrates were prepared by the reported methods.[2,7] The chiral diamines (pn and chxn) were set free from the corresponding tartrates and used in situ according to the method reported by us.[7] In a typical experiment, the ethanol solution of pn (0.01 mol) was mixed with HACP (0.02 mol) in ethanol solution and stirred at reflux for 6 h.[8] The yellow solution of the Schiff base was evaporated to dryness and recrystallized from dichloromethane.

An appropriate amount of the chiral Schiff bases (1 mmol) dissolved in methanol was allowed to reflux under an inert atmosphere with $Ni(OAc)_2{\cdot}4H_2O$ (1 mmol) in the presence of triethylamine (1 mmol) for 30 min (Scheme 1). The solution was filtered and concentrated till dryness. The resulting residue was washed in ethanol and dried in vacuum. The overall yields for the complexes were in the range of 65–70%.

We attempted to obtain suitable crystals of all the complexes by recrystallization from methanol for X-ray analysis. The X-ray crystal structure of HACP-(*R*)-pn-Ni(II) $\mathbf{1a}^{R}$, HACP-(*RR*)-chxn-Ni(II) $\mathbf{1b}^{RR}$, and HACP-(*SS*)-dpen-Ni(II) $\mathbf{1c}^{SS}$ are depicted in Figure 1. The crystal structure of HACP-(*RR*)-chxn-Ni(II) $\mathbf{1b}^{RR}$ has been reported by Szlyk et al.[8]

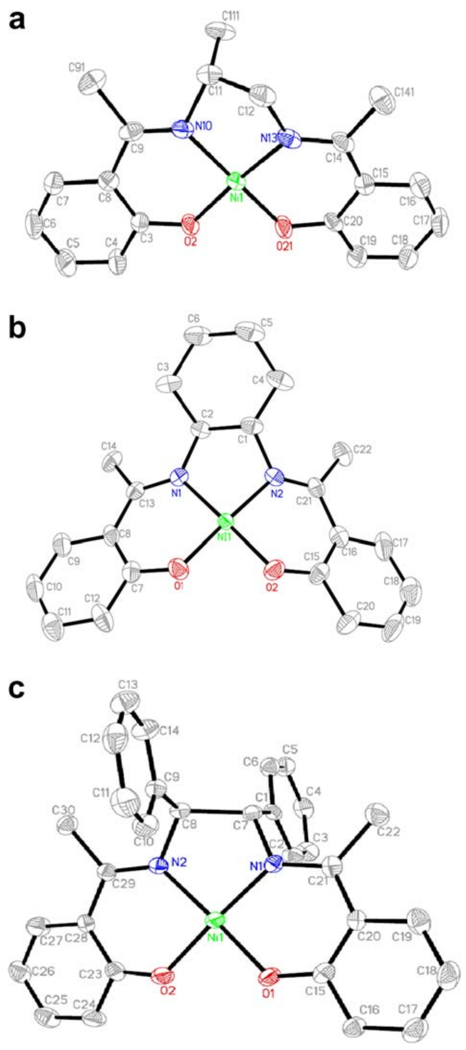
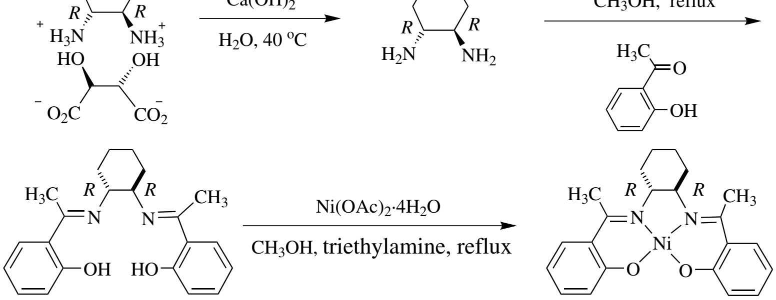


Figure 1. Molecular structures of the complexes $\mathbf{1a}^{R}$ (a), $\mathbf{1b}^{RR}$ (b), and $\mathbf{1c}^{SS}$ (c).

There are two molecules in asymmetric unit in the complexes $\mathbf{1a}^{R}$ and $\mathbf{1b}^{RR}$. The nearly planar coordination sphere of each Ni(II) is slightly tetrahedrally distorted (Fig. 2), with the maximum deviation of 0.0817 Å from the best coordination plane. The Ni(II) ion is −0.0188 Å away from the best coordination plane in $\mathbf{1a}^{R}$ and −0.0028 Å in $\mathbf{1c}^{SS}$, while in $\mathbf{1b}^{RR}$ it is −0.029 Å. The distortions observed of the coordination sphere can be related to the geometric constrictions imposed by two methyl groups



Scheme 1. Synthesis of HACP-*RR*-chxn and its Ni(II) complexes.

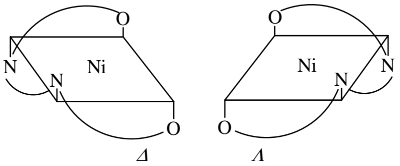


Figure 2. Illustration of tetrahedral distortion in the Ni(II) Schiff base complexes.

of the ligand in both the reported complexes and the (*R*,*S*)-analogue.[8,9] In both molecules, the deviations from the best plane Ni–O–N–N–O are small, but statistically significant. We have analyzed these molecular structures and found the sinistral disposition along the pseudo-C_2 axis for $\mathbf{1a}^R$, that is, the Λ configuration around the metal ion.[5a] The dextral disposition was found in $\mathbf{1c}^{SS}$, so its absolute configuration is decided as Δ.

The UV–vis spectrum of each complex shows a weak d–d band maximum at about 550 ($\varepsilon = 200$–400) nm. This band is interpreted as transitions from the weak σ-antibonding 3d orbital, to the strongly σ-antibonding 3d orbital. The azomethine π–π* transition bands lie near 320 ($\varepsilon = 3000$–7000) nm. The higher energy bands near 300 ($\varepsilon > 10^5$) nm are considered to be charge transfer bands, where electronic transitions may take place from internal ligand π orbitals and non-bonding oxygen orbitals to the strongly antibonding 3d orbital.[4a,8]

The CD spectra of the (*S*,*S*)-ligands are approximately mirror images of those of their respective (*R*,*R*)-enantiomers. Some CD spectra of the complexes are given in Figures 3 and 4, in which the bands around 550 nm with opposite Cotton effects are assigned to d–d transition, while the d–π* band lies near 365 nm and 440 nm. The π–π* transition in the ligands lies in the higher frequency region from 332 nm to 346 nm.[5]

We have compared X-ray single crystal structure measurement and CD spectroscopy. In the HACP-(*SS*)-dpen-Ni(II) $\mathbf{1c}^{SS}$, for example, when its X-ray crystal structure shows the dextral disposition along the pseudo-C_2 axis, that is, Δ configuration, the corresponding d–d transition band at 554 nm exhibits a positive Cotton effect. For the complexes derived from HACP and DHA, the two exciton components can be predicted to have analogous CD spectra, because all of them have methyl substituents on the ethylene moiety.[8,9] In addition, both of the chelate rings around the metal center are six-membered and five-membered, respectively. As a result, we can compare the CD spectra of these two series of complexes not only in the UV region but also in the d–d visible region. By means of the exciton chirality method,[6] the exciton couplet in the UV region roughly suggests the conformation for pseudo-planar coordination environment. According to IUPAC nomenclature, the two conformations of each pair of the sal-diamine complexes are Δλ or Λδ,[4c] where lower-case symbols reflect the chirality (or conformation) of the ethylene-diamine chelate ring and the up-case symbols that of the tetrahedral distortion of the metal coordination (i.e., configuration). Thus, the conformation would imply chirality Δλ for the HACP-(*S*)-pn and HACP-*SS*-dpen derivatives and chirality Λδ for the HACP-*SS*-chxn derivatives with a concomitant inversion of the Cotton effects. These results seem to agree with the predictions on chiral quadridentate sal-diamine complexes reported by Pasini.[4c]

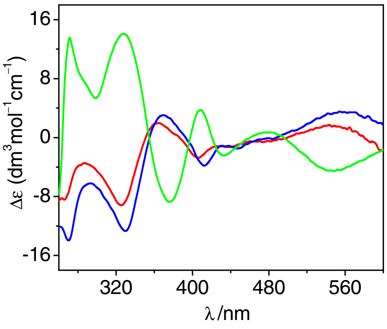


Figure 3. CD spectra of complexes HACP-(*SS*)-diamine-Ni(II): HACP-(*S*)-pn-Ni(II) (red), HACP-(*SS*)-chxn-Ni(II) (green), HACP-(*SS*)-dpen-Ni(II) (blue).

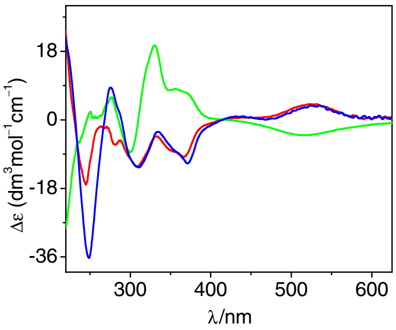


Figure 4. CD spectra of complexes DHA-(*SS*)-diamine-Ni(II): DHA-(*S*)-pn-Ni(II) (red), DHA-(*SS*)-chxn-Ni(II) (green), DHA-(*SS*)-dpen-Ni(II) (blue).

However, for the second series derived from DHA, there are several chromophores such as C=C, C=O, etc. in the six-membered heteroatomic ring, and their energy levels are close to that of the azomethine chromophore. The certain exciton couplet in the UV region was not observed, because one of its components is cancelled by the overlapping of some other bands.[4c] Therefore, the exciton chirality method[6] is somewhat unreliable for this series. On the other hand, the obvious CD bands corresponding to d–d transition were observed in the 500–600 nm range and there is a unanimous agreement between the CD pattern and the absolute configuration for both series of the chiral Ni(II) Schiff base complexes discussed above. These are tabulated in Table 1.

Within these two series, all the complexes derived from the diamines with same configuration show the same sign of CD pattern at the d–d transition region except for chxn which displays opposite behavior.[4] The reason for this exception is the requirements of the two fused rings, which means that the rigidity of the rings dictates the most stable Λδ chirality. Thus, a good correlation holds within these two series between the sign of the CD band in the visible range and the absolute configuration about the metal ion.

Table 1. Absolute configuration of the complexes and corresponding CD sign in the 500–600 nm range

Entry	Complex	Configuration	CD sign
1	HACP-(*S*)-pn-Ni(II)	Δ	+
2	HACP-(*R*)-pn-Ni(II)	Λ	−
3	HACP-(*SS*)-chxn-Ni(II)	Λ	−
4	HACP-(*RR*)-chxn-Ni(II)	Δ	+
5	HACP-(*SS*)-dpen-Ni(II)	Δ	+
6	HACP-(*RR*)-dpen-Ni(II)	Λ	−
7	DHA-(*S*)-pn-Ni(II)	Δ	+
8	DHA-(*R*)-pn-Ni(II)	Λ	−
9	DHA-(*SS*)-chxn-Ni(II)	Λ	−
10	DHA-(*RR*)-chxn-Ni(II)	Δ	+
11	DHA-(*SS*)-dpen-Ni(II)	Δ	+
12	DHA-(*RR*)-dpen-Ni(II)	Λ	−

In addition, the solution CD spectra were also compared with solid-state CD spectra of some Ni(II) Schiff base complexes. Our study has revealed that the chiral complexes maintain the same configuration found in solution states.[10]

3. Conclusion

In conclusion, on comparison of the CD spectra of these two series, the CD signal in the d–d transition region is useful as a reference to determine the absolute configuration of the complexes. In the case of tetra-coordinated pseudo-planar Ni(II) complexes we therefore have the following empirical rule: (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 Cotton effects around 550 nm; and (ii) $(S)\Lambda\delta$ for the HACP-(*SS*)-chxn, DHA-(*SS*)-chxn derivatives with a concomitant inversion of the Cotton effects. It can be used as a diagnosis to assign the absolute configuration of some tetrahedral or pseudo-planar Schiff base complexes with the similar electronic configuration and coordination sphere. 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 Schiff base complexes. 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 purification. Infrared spectra (KBr pellets) were recorded on a Nicolet 370 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 Varian UNITY 500M NMR spectrometer in $CDCl_3$ using tetra-methylsilane 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. Crystal structure analysis was carried out on a Bruker APEX CCD diffractometer.

4.2. *N*,*N*′-(1*S*)-(+)-1,2-propylenebis(2-hydroxyacetophenonylideneiminato)nickel(II) 1a^{S}

A brick red solid, 0.14 g, 76.3%, mp > 300 °C. IR(KBr): v 2928 ($-CH_3$), 1601 (C=N), 1135 (C–N), 1359 (C–O), 532 (Ni–N), 451 (Ni–O) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 500 MHz, ppm): 1.47 (3H, d, $J = 8.5$ Hz, CH_3), 2.06 (3H, s, CH_3), 2.11 (3H, s, CH_3), 3.04 (1H, m, CH), 3.64 (H, s, CH_2), 3.96 (H, s, CH_2), 6.44 (H, d, $J = 7.0$ Hz, Ar), 6.50 (H, d, $J = 7.0$ Hz, Ar), 7.14 (6H, m, Ar). Anal. Calcd for $C_{19}H_{20}N_2O_2Ni$: requires: C, 62.17; H, 5.49; N, 7.63. Found: C, 62.60; H, 5.52; N, 7.55.

4.3. *N*,*N*′-(1*S*,2*S*)-(+)-1,2-cyclohexylenebis(2-hydroxyacetophenonylideneiminato)nickel(II) 1b^{SS}

This is a known compound.[8] A brick red solid, 1.70 g, 83.5%, mp > 300 °C. IR(KBr): v 2927 ($-CH_3$), 1601 (C=N), 1162 (C–N), 1358 (C–O), 529 (Ni–N), 472 (Ni–O) cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_2O_2Ni$: requires: C, 64.90; H, 5.94; N, 6.88. Found: C, 64.61; H, 5.86; N, 6.44.

4.4. *N*,*N*′-(1*R*,2*R*)-(+)-1,2-diphenylethylenebis(2-hydroxyacetophenonylideneiminato)nickel(II) 1c^{RR}

A brick red solid, 0.19 g, 74.2%, mp > 300 °C. IR(KBr): v 2927 ($-CH_3$), 1573 (C=N), 1162 (C–N), 1349 (C–O), 521 (Ni–N), 460 (Ni–O) cm^{-1}. Anal. Calcd for $C_{30}H_{26}N_2O_2Ni$: requires: C, 71.32; H, 5.19; N, 5.54. Found: C, 71.57; H, 5.33; N, 5.45.

4.5. *N*,*N*′-(1*S*)-(+)-1,2-propylenebis{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine}nickel(II) 2a^{S}

This is a known compound.[3] A red solid, 0.16 g, 75.8%, mp > 300 °C. IR(KBr): v 2923 ($-CH_3$), 1571 (C=N), 1046 (C–N), 1353 (C–O), 548 (Ni–N), 486 (Ni–O) cm^{-1}. Anal. Calcd for $C_{19}H_{20}N_2O_6Ni$: requires: C, 53.01; H, 4.69; N, 6.51. Found: C, 53.05; H, 4.65; N, 6.49.

4.6. *N*,*N*′-(1*R*,2*R*)-(−)-1,2-cyclohexylenebis{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine}nickel(II) 2b^{RR}

This is a known compound.[3] A red solid, 0.18 g, 76.2%, mp > 300 °C. IR(KBr): v 2927 ($-CH_3$), 1572 (C=N), 1067 (C–N), 1346 (C–O), 544 (Ni–N), 454 (Ni–O) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 500 MHz, ppm): 1.21–1.67 (8H, m, $(CH_2)_4$), 1.96 (6H, s, CH_3), 2.41 (6H, s, CH_3), 3.66 (2H, s, CH), 5.64 (2H, s, CH). Anal. Calcd for $C_{22}H_{24}N_2O_6Ni$: requires: C, 56.09; H, 5.13; N, 5.95. Found: C, 56.73; H, 5.54; N, 5.59.

4.7. *N*,*N*′-(1*R*,2*R*)-(+)-1,2-diphenylethylenebis{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine}nickel(II) 2c^{RR}

This is a known compound.[3] A red solid, 0.21 g, 72.6%, mp > 300 °C. IR(KBr): v 2927 ($-CH_3$), 1554 (C=N), 1085 (C–N), 1354 (C–O), 551 (Ni–N), 423 (Ni–O) cm^{-1}. Anal.

Calcd for $C_{30}H_{26}N_2O_6Ni$: requires: C, 63.30; H, 4.60; N, 4.92. Found: 63.13; H, 4.72; N, 4.90.

4.8. X-ray structure analysis

Diffraction data were obtained on a Bruker APEX CCD diffractometer, using graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structures were solved by direct methods with the program SHELXS-97.[11] Full matrix least-squares refinement was carried out with SHELXL-97.[12]

Crystal data for $C_{38}H_{40}Ni_2N_4O_4$ **1a**^{R}: Orthorhombic, $P2_12_12_1$, $a = 10.340(3)$ Å, $b = 12.506(3)$ Å, $c = 25.369(6)$ Å, $V = 3280.4(14)$ Å^3, $Z = 4$, $D_{calcd} = 1.487$ mg cm^{-3}, $T = 296(2)$ K, $R_1 = 0.0749$, $\omega R_2 = 0.1566[I > 2\sigma(I)]$, $R_1 = 0.0908$, $\omega R_2 = 0.1641$ for all data.

Crystal data for $C_{30}H_{26}NiN_2O_2$ **1c**^{SS}: Orthorhombic, $P2_12_12_1$, $a = 9.8609(7)$ Å, $b = 12.0490(9)$ Å, $c = 20.6027(14)$ Å, $V = 2447.9(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.371$ mg cm^{-3}, $T = 223(2)$ K, $R_1 = 0.0466$, $\omega R_2 = 0.0877[I > 2\sigma(I)]$, $R_1 = 0.0743$, $\omega R_2 = 0.0969$ for all data.

Crystal data for $C_{44}H_{48}Ni_2N_4O_4$ **1b**^{RR}: Orthorhombic, $P2_12_12_1$, $a = 8.895(3)$ Å, $b = 9.099(3)$ Å, $c = 22.632(6)$ Å, $V = 1831.7(9)$ Å^3, $Z = 2$, $D_{calcd} = 1.477$ mg cm^{-3}, $T = 296(2)$ K, $R_1 = 0.0565$, $\omega\ R_2 = 0.1194[I > 2\sigma(I)]$, $R_1 = 0.0640$, $\omega R_2 = 0.1234$ for all data.

Crystallographic data (excluding structure factors) for the structures of **1a**^{R} and **1c**^{SS} in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 270604 and 242628. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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