

# Nickel Complexes with N<sub>2</sub>O Donor Ligands: Syntheses, Structures, Catalysis and Magnetic Studies

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Two new terephthalato-bridged tetranuclear polymeric Ni<sup>II</sup> complexes, namely [Ni<sub>4</sub>L<sub>4</sub><sup>1</sup>(μ-tp-κ<sub>4</sub>-O)(H<sub>2</sub>O)<sub>2</sub>(μ-tp-κ<sub>2</sub>-O)]·2C<sub>2</sub>H<sub>5</sub>OH·CH<sub>3</sub>OH·3H<sub>2</sub>O (**1**) and [Ni<sub>4</sub>L<sub>4</sub><sup>2</sup>(μ-tp-κ<sub>4</sub>-O)(H<sub>2</sub>O)<sub>2</sub>(μ-tp-κ<sub>2</sub>-O)]·3H<sub>2</sub>O (**2**) [L<sup>1</sup> = *N*-(3-aminopropyl)-5-bromosalicylaldehyde and L<sup>2</sup> = *N*-(3-aminopropyl)salicylaldehyde], are reported along with the syntheses and structures of the dicyanoargentate-bridged polymeric complexes [Ni(L<sup>1</sup>)(H<sub>2</sub>O)-{Ag(CN)<sub>2</sub>}]<sub>n</sub> (**3**) and [Ni(L<sup>3</sup>)(MeOH){Ag(CN)<sub>2</sub>}]<sub>n</sub> (**4**) [L<sup>3</sup> = *N*-(3-amino-2,2-dimethylpropyl)-5-bromosalicylaldehyde]. All four

complexes are found to be effective heterogeneous catalysts for the epoxidation of alkenes such as styrene, *α*-methylstyrene and cyclohexene in the presence of *tert*-butyl hydroperoxide. The variable-temperature magnetic susceptibility measurements (300–2 K) of complex **1** show a fair degree of antiferromagnetic coupling between the Ni<sup>II</sup> centers.

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## Introduction

Low-dimensional coordination polymers, including one-dimensional (1D) chain-like and two-dimensional (2D) layer-like structures, have received much attention in recent years owing to their intriguing structural features and unique electroconductive, nonlinear optical, and magnetic properties, which differ from those of three-dimensional (3D) coordination polymers.<sup>[1]</sup> A great variety of low-dimensional coordination polymers based on d-block transition metal ions and organic ligands have been prepared to date, many of which have potential applications in the field of functional materials.<sup>[2–6]</sup> The organic components containing N- or O- donors in the framework offer great potential for chemical and structural diversity.<sup>[7]</sup>

Organic aromatic polycarboxylates are some of the most widely employed multidentate O-donor ligands for the preparation of such coordination polymers with multidimensional networks. In this respect, terephthalate (tp) has been studied extensively as a rigid and versatile bridging ligand<sup>[8]</sup> as it contains multiple bridging moieties that lead

to a variety of connection modes with transition metal centers and provide abundant structural motifs. Furthermore, it can act not only as a hydrogen-bond donor but also as an acceptor due to the existence of protonated and/or deprotonated carboxylate groups. The terephthalate ligand is therefore regarded as an excellent candidate for the construction of multidimensional coordination frameworks.

The introduction of another kind of both N- and O-donor chelating ligand, such as a tridentate Schiff base, in the {M/tp} (M = transition metal) system may induce new structural evolution as the introduction of N-donor chelating ligands into the metal sites may inhibit the expansion of the polymeric frameworks and lead to the desired low-dimensional coordination polymers. However, the synthesis of complexes containing mixed ligands is expected to be more difficult to control than that of complexes containing one ligand for several reasons, such as the different solubility of the organic ligands and competition between these ligands to coordinate the transition metal. In order to gain insight into the parameters that control these variables we have synthesized two new terephthalate-bridged tetranuclear polymeric Ni<sup>II</sup> complexes, namely [Ni<sub>4</sub>L<sub>4</sub><sup>1</sup>(μ-tp-κ<sub>4</sub>-O)(H<sub>2</sub>O)<sub>2</sub>(μ-tp-κ<sub>2</sub>-O)]·2C<sub>2</sub>H<sub>5</sub>OH·CH<sub>3</sub>OH·3H<sub>2</sub>O (**1**) and [Ni<sub>4</sub>L<sub>4</sub><sup>2</sup>(μ-tp-κ<sub>4</sub>-O)(H<sub>2</sub>O)<sub>2</sub>(μ-tp-κ<sub>2</sub>-O)]·3H<sub>2</sub>O (**2**); L<sup>1</sup> = *N*-(3-aminopropyl)-5-bromosalicylaldehyde and L<sup>2</sup> = *N*-(3-aminopropyl)salicylaldehyde]. Ni<sup>II</sup> forms a phenolate-bridged binuclear unit in these complexes and two such units are connected by a terephthalate moiety to form a tetranuclear nickel(II) complex. The crystal structure of complex **1** shows that the tetranuclear units are connected to each other by the terephthalate moiety in a bis(monodentate) mode to form a one-dimensional network. The variable-

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temperature magnetic behavior of complex **1** is also investigated.

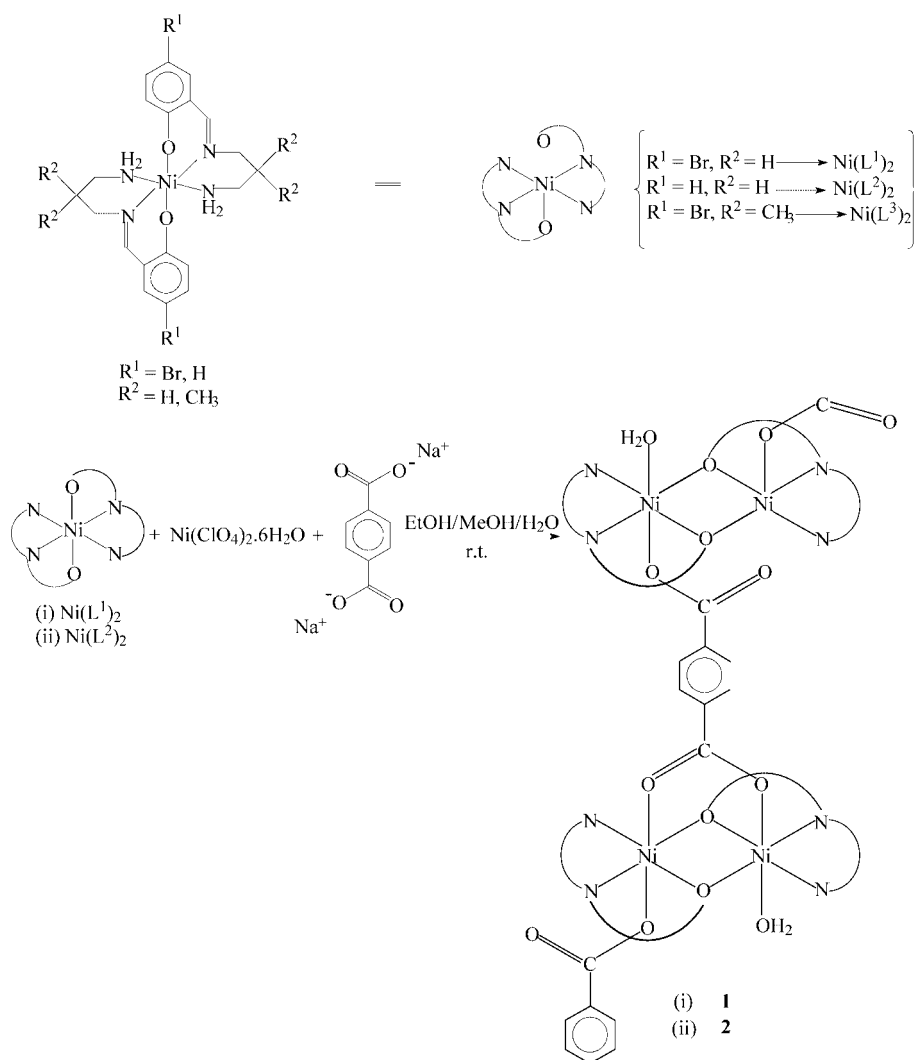
Like terephthalate, cyanometalate anions have been extensively used as building blocks in supramolecular coordination polymers.<sup>[9,10]</sup> Compared to the higher coordination counterparts of various transition metals, there has been considerably less investigation of two-coordinate linear cyanometalate building blocks for the construction of coordination polymers. We have chosen to examine the ability of the linear dicyanoargentate ion  $[\text{Ag}(\text{CN})_2]^-$  to form supramolecular frameworks. The syntheses and structures of two dicyanoargentate-bridged polymeric networks, namely  $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})\{\text{Ag}(\text{CN})_2\}]_a$  (**3**) and  $[\text{Ni}(\text{L}^3)(\text{MeOH})\{\text{Ag}(\text{CN})_2\}]_a$  (**4**;  $\text{L}^3 = N$ -(3-amino-2,2-dimethylpropyl)-5-bromosalicylaldehyde), are therefore also included in this paper.

Intrigued by a recent study concerning the use of (salen)- $\text{Ni}^{\text{II}}$  complexes as homogeneous/heterogeneous epoxidation catalysts,<sup>[11]</sup> we extended our study to the epoxidation of alkenes such as styrene,  $\alpha$ -methylstyrene and cyclohexene in the presence of *tert*-butyl hydroperoxide heterogeneously catalyzed by complexes **1–4**.

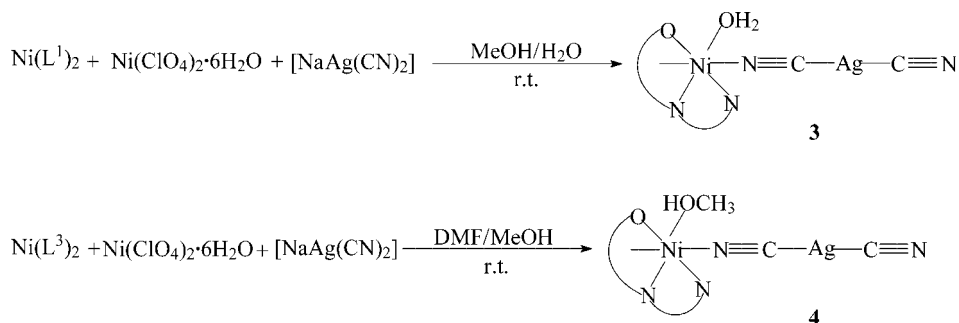
## Results and Discussion

### Synthesis

The monocondensed ligands  $\text{L}^1$ – $\text{L}^3$  were prepared as their nickel complexes  $\text{Ni}(\text{L}^1)_2$ ,  $\text{Ni}(\text{L}^2)_2$ , and  $\text{Ni}(\text{L}^3)_2$  by treating 5-bromosalicylaldehyde or salicylaldehyde with  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and the corresponding amine (see Experimental Section). Complex **1** was prepared by the reaction of  $\text{Ni}(\text{L}^1)_2$  with equimolar amounts of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the disodium salt of terephthalic acid in EtOH/MeOH/ $\text{H}_2\text{O}$  to produce the  $\mu_2$ -phenolate and terephthalate-bridged tetranuclear complex  $[\text{Ni}_4\text{L}_4^1(\mu\text{-tp-}\kappa_4\text{-O})(\text{H}_2\text{O})_2(\mu\text{-tp-}\kappa_2\text{-O})] \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$  (Scheme 1). Complex **2** was prepared in the same way as described for complex **1** but with salicylaldehyde for the Schiff base condensation instead of 5-bromosalicylaldehyde. Complex **3** was prepared by the reaction of  $\text{Ni}(\text{L}^1)_2$  with equimolar amounts of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $[\text{NaAg}(\text{CN})_2]$  in MeOH/ $\text{H}_2\text{O}$  to produce the argentocyanide-bridged heterobinuclear polymeric complex  $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})\{\text{Ag}(\text{CN})_2\}]_a$  (Scheme 2). Complex **4** was syn-



Scheme 1. Synthetic routes to complexes **1** and **2**.

Scheme 2. Synthetic routes to complexes **3** and **4**.

thesized in dmf/MeOH by treating Ni(L<sup>3</sup>)<sub>2</sub> with equimolar amounts of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and [NaAg(CN)<sub>2</sub>] to yield the argentocyanide-bridged polymeric species [Ni(L<sup>3</sup>)(MeOH)-{Ag(CN)<sub>2</sub>}]<sub>n</sub>.

### IR Spectra

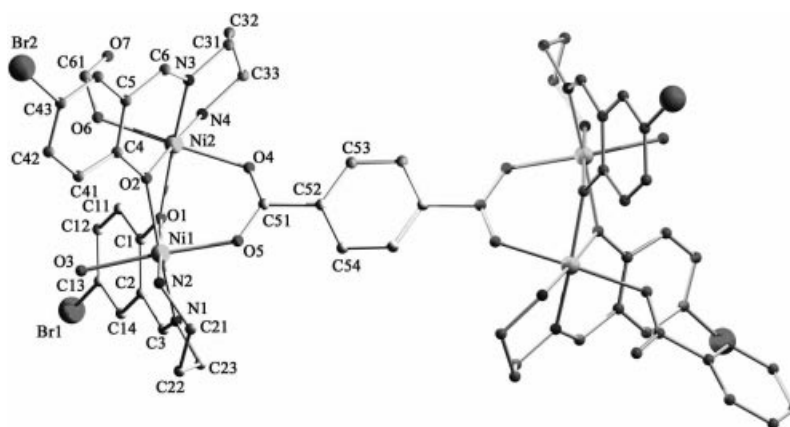
The IR spectra of **1** and **2** show a broad absorption band in the range 3321–3504 cm<sup>−1</sup> which can be assigned to the O–H stretching vibrations of the coordinated and noncoordinated water molecules and noncoordinated MeOH and EtOH molecules in the case of complex **1**. The strong band in the range 1637–1645 cm<sup>−1</sup> can be assigned to ν(CN<sub>iminic</sub>), which suggests coordination of the ligands to the metal centers through the imine nitrogen atoms. The tp unit coordinates the metal ions in both complexes in both its bis(monodentate) and bis(bidentate) coordination modes. The values of Δν, indicating the difference between the asymmetric stretching ν<sub>a</sub>(COO<sup>−</sup>) and the symmetric stretching ν<sub>s</sub>(COO<sup>−</sup>), for **1** are 148 and 29 cm<sup>−1</sup>, whereas those for complex **2** are 142 and 27 cm<sup>−1</sup>.

The strong band at 2162 cm<sup>−1</sup> in the IR spectrum of complex **3** is due to the ν(CN) absorption of the N-bonded argentocyanide unit and the band at 3346 cm<sup>−1</sup> is due to the water molecule coordinated to the Ni<sup>II</sup> center. Complex **4** also exhibits a strong band at 2164 cm<sup>−1</sup> due to the N-bonded argentocyanide unit. The broad band at 3437 cm<sup>−1</sup> is assigned to an O–H stretching vibration, thereby con-

firmed the presence of the coordinated CH<sub>3</sub>OH molecule. The strong band in the range 1585–1602 cm<sup>−1</sup> observed for all complexes is due to the ν(CO) absorption of the phenolate-containing ligands.

### Structure of Complex 1

A view of **1** is shown in Figure 1 and key bond lengths and angles are listed in Table 1. The crystal structure of this complex shows that the asymmetric unit contains a tetranuclear molecule of the type [Ni<sub>4</sub>L<sub>4</sub><sup>1</sup>(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>-(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)] in addition to two ethanol, one methanol, and three water molecules. The tetranuclear unit is formed by two Ni<sup>II</sup> atoms (Ni1 and Ni2) bridged by two μ<sub>2</sub>-phenolato oxygen atoms (O1 and O2) of the Schiff-base ligands and a terephthalato ligand in its bis(bidentate) mode that connects the four Ni<sup>II</sup> centers. The tridentate ligand L<sup>1</sup> provides an N<sub>2</sub>O<sub>2</sub> donor set around each metal atom. The basal NiN<sub>2</sub>O<sub>2</sub> plane for the Ni1 center is formed by the two nitrogen atoms (N1 and N2) and the two oxygen atoms (O1 and O2) of the bridging phenolato ligands while the basal plane of the Ni2 center is formed by two different nitrogen atoms (N3 and N4) of another L<sup>1</sup> ligand and the same phenolate oxygens (O1 and O2). The O3 atom of the terminal water molecule and the O5 atom of the bridging bis(bidentate) terephthalato ligand occupy the axial positions of the Ni1 center. The coordination environment of the Ni2 center is somewhat different to that of the Ni1 center. Thus, for

Figure 1. A view of the molecule of complex **1**.

the Ni2 center the axial positions are occupied by the O4 atom of the bridging terephthalato ligand and the O6 atom of another bridging terephthalato ligand in its bis(monodentate) coordination mode. Each nickel atom has a distorted octahedral environment. The phenolate-bridged nickel atoms are separated by 3.076 Å with two Ni1–O1–Ni2 and Ni1–O2–Ni2 bridging angles of 97.4(4)° and 96.5(3)°, respectively; two Ni<sub>2</sub>N<sub>4</sub>O<sub>2</sub> moieties are separated from each other by 10.996 Å. The basal bond lengths around Ni1 are within the range 2.020(8)–2.089(10) Å while those around Ni2 are in the range 2.044(8)–2.092(10) Å. The apical Ni1–O3, Ni1–O5, Ni2–O4, and Ni2–O6 bond lengths are 2.143(6), 2.077(8), 2.091(6), and 2.133(8) Å, respectively. The O3–Ni1–O5 bond angle is 176.8(3)° while that for O4–Ni2–O6 is 177.8(3)°. The Ni–O<sub>tp</sub> bond lengths are similar to those found in other terephthalate-bridged nickel complexes.<sup>[12,13]</sup>

The packing diagram of complex **1** (Figure 2) shows that the tetranuclear Ni<sup>II</sup> units are joined to each other by the

terephthalate moiety in its bis(monodentate) mode to form an infinite one-dimensional network where symmetry-related O6 terephthalato-oxygen atoms bind two Ni2 centers in a zig-zag structure along the *a*-axis. The simultaneous presence of two terephthalate ligands with different bridging modes gives rise to an unprecedented coordination chain. It is interesting to note that the adjacent layers are not parallel when viewed along the *c*-axis but are inclined to each other with an angle of 39.17° (Figure 3). The dihedral angle formed between the anion and the equatorial plane is 62.14°, and the carboxylate group O6/C61/O7 deviates from coplanarity with the phenyl ring (11.65°). This deviation is uniform throughout the chain. The Ni...Ni separation within a linear chain is 11.296 Å. This distance is

Table 1. Selected bond lengths [Å] and angles [°] in complex **1**.

| Bond lengths [Å] |           |            |           |
|------------------|-----------|------------|-----------|
| Ni1–O1           | 2.020(8)  | Ni2–O1     | 2.075(8)  |
| Ni1–O2           | 2.079(8)  | Ni2–O2     | 2.044(8)  |
| Ni1–O3           | 2.143(6)  | Ni2–O4     | 2.091(6)  |
| Ni1–O5           | 2.077(8)  | Ni2–O6     | 2.133(8)  |
| Ni1–N1           | 2.030(11) | Ni2–N3     | 2.047(10) |
| Ni1–N2           | 2.089(10) | Ni2–N4     | 2.092(10) |
| Bond angles [°]  |           |            |           |
| O1–Ni1–O2        | 79.7(3)   | O1–Ni2–O2  | 79.2(3)   |
| O1–Ni1–O3        | 88.0(3)   | O1–Ni2–O4  | 86.8(3)   |
| O1–Ni1–O5        | 94.5(3)   | O1–Ni2–O6  | 95.4(3)   |
| O1–Ni1–N1        | 89.0(4)   | O1–Ni2–N3  | 165.5(4)  |
| O1–Ni1–N2        | 174.6(4)  | O1–Ni2–N4  | 97.0(3)   |
| O2–Ni1–O3        | 93.9(3)   | O2–Ni2–O4  | 93.0(3)   |
| O2–Ni1–O5        | 88.7(3)   | O2–Ni2–O6  | 86.9(3)   |
| O2–Ni1–N1        | 168.6(4)  | O2–Ni2–N3  | 87.6(4)   |
| O2–Ni1–N2        | 94.9(4)   | O2–Ni2–N4  | 176.3(3)  |
| O3–Ni1–O5        | 176.8(3)  | O4–Ni2–O6  | 177.8(3)  |
| O3–Ni1–N1        | 86.9(4)   | O4–Ni2–N3  | 87.7(4)   |
| O3–Ni1–N2        | 92.8(3)   | O4–Ni2–N4  | 86.3(4)   |
| O5–Ni1–N1        | 91.0(4)   | O6–Ni2–N3  | 90.1(3)   |
| O5–Ni1–N2        | 85.0(4)   | O6–Ni2–N4  | 93.9(3)   |
| N1–Ni1–N2        | 96.5(4)   | N3–Ni2–N4  | 96.0(4)   |
| Ni1–O1–Ni2       | 97.4(4)   | Ni1–O2–Ni2 | 96.5(3)   |

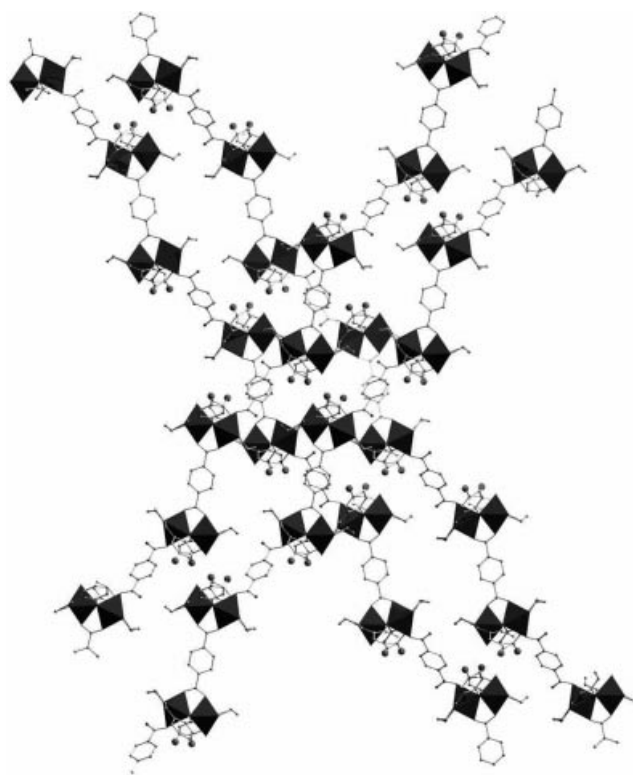


Figure 3. A view of the packing fragment showing the crossing of the 1D networks in **1**. The polyhedra represent the Ni<sub>2</sub>N<sub>4</sub>O<sub>6</sub> core.

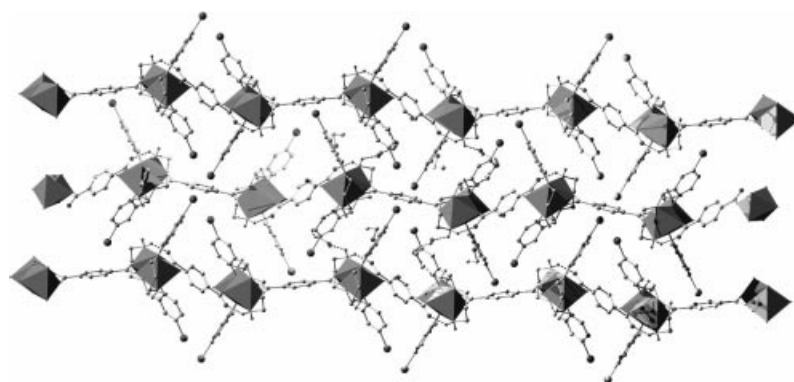


Figure 2. Packing diagram of complex **1**. The polyhedra represent the Ni<sub>2</sub>N<sub>4</sub>O<sub>6</sub> core.

shorter than in other terephthalate-bridged nickel complexes such as [Ni(pyrazole)<sub>4</sub>(tp)]<sub>n</sub> [11.446(2) Å],<sup>[14]</sup> [Ni(C<sub>12</sub>H<sub>30</sub>N<sub>6</sub>O<sub>2</sub>)(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sub>n</sub>·4nH<sub>2</sub>O] [11.514(1) Å],<sup>[12]</sup> where *n* is ∞, and [(μ-terephthalato){Ni(dca)(dpt)(H<sub>2</sub>O)}<sub>2</sub>] [11.379(10) Å].<sup>[15]</sup> The one-dimensional chains are connected together by intermolecular hydrogen-bonding interactions between the oxygen atom of uncoordinated methanol and the coordinated amine of the Schiff base [N2...O300 3.33(3) Å]. In addition, one lattice ethanol molecule takes part in hydrogen bonding with another coordinated amine group of the Schiff base [N4...O200 3.12(3) Å]. There is also an intramolecular hydrogen bond connecting an amine group with a bis(monodentate) terephthalato oxygen atom [N4...O7 2.889(14) Å]. The two C–O bond lengths of the carboxylate group are practically identical even though one is coordinated to the Ni2 center [1.253(16) Å] and the other is not [1.253(19) Å]. In general, the C–O bond lengths of coordinated carboxylate groups fall in the range 1.266–1.279 Å and are longer than the free carbonyl C–O bonds (1.226–1.255 Å) when terephthalate coordinates a metal ion in a monodentate fashion.<sup>[12]</sup>

### Structure of Complex 3

The coordination environment of the Ni<sup>II</sup> ion in complex **3** is shown in Figure 4 along with the atom-numbering scheme. Key bond lengths and angles are listed in Table 2. The coordination environment for each nickel center is best described by a distorted octahedral geometry. Two nitrogen atoms, a phenolate oxygen atom of the tridentate Schiff-base ligand L<sup>1</sup>, and an oxygen atom of the coordinated water molecule, with Ni1–N1, Ni1–N2, Ni1–O1, and Ni1–O2 distances of 2.045(4), 2.076(5), 2.015(4), and 2.152(4) Å, respectively, define the equatorial plane around the nickel atom. The axial sites are occupied by two nitrogen atoms of the bridging argentocyanide moiety with Ni1–N3 and Ni1–N4 bond lengths of 2.115(5) and 2.101 Å, respectively.

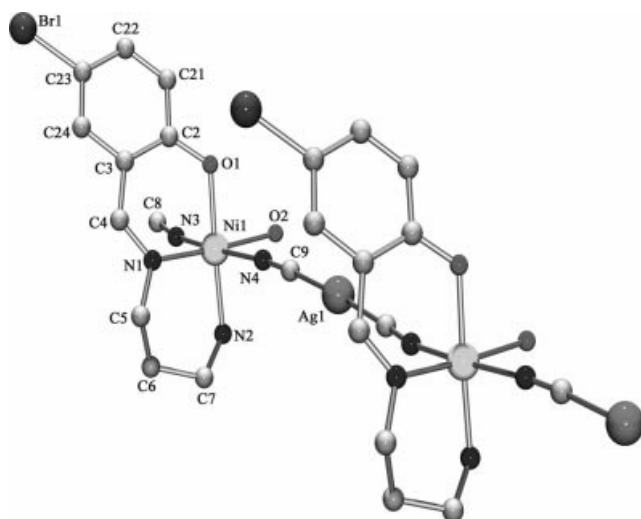


Figure 4. A view of the molecule of complex **3**.

The central nickel atom lies slightly above the equatorial plane (0.048 Å).

Table 2. Selected bond lengths [Å] and angles [°] in complex **3**.

| Bond lengths [Å]      |            |           |           |
|-----------------------|------------|-----------|-----------|
| Ni1–O1                | 2.015(4)   | N3–C8     | 1.142(9)  |
| Ni1–O2                | 2.152(4)   | Ag1–C8    | 2.064(7)  |
| Ni1–N1                | 2.045(4)   | Ag1–C9    | 2.065(7)  |
| Ni1–N2                | 2.076(5)   | N4–C9     | 1.139(9)  |
| Ni1–N3                | 2.115(5)   |           |           |
| Bond angles [°]       |            |           |           |
| O1–Ni1–O2             | 87.66(16)  | O1–Ni1–N1 | 89.90(18) |
| O1–Ni1–N2             | 175.28(17) | O1–Ni1–N3 | 86.61(19) |
| O2–Ni1–N1             | 175.72(19) | O2–Ni1–N2 | 87.91(17) |
| O2–Ni1–N3             | 84.29(17)  | N1–Ni1–N2 | 94.42(19) |
| N1–Ni1–N3             | 92.05(19)  | N2–Ni1–N3 | 91.4(2)   |
| C8–Ag1–C9             | 176.4(3)   |           |           |
| Hydrogen bonds [Å, °] |            |           |           |
| D–H...A               | D...A      | H...A     | ∠D–H...A  |
| O2–H2...O1            | 2.608(6)   | 1.78(5)   | 176(7)    |

The crystal packing of complex **3** (Figure 5) shows that the [Ag(CN)<sub>2</sub>]<sup>−</sup> units display an almost linear coordination [C8–Ag1–C9 176.4(3)°] with Ag1–C8 and Ag1–C9 bond lengths of 2.064(7) and 2.065(7) Å, respectively, and form endless one-dimensional chains involving the [NiL<sup>1</sup>(H<sub>2</sub>O)]<sup>+</sup> moiety. These chains lie parallel to each other with diagonal distances *a* and *b* of 8.12 and 5.95 Å, respectively, and an Ag...Ag distance of about 10.6 Å. The minimum Ag...Ag distance found between two successive layers is 4.514 Å, which is greater the van der Waals diameter of silver (3.44 Å)<sup>[16]</sup> and hence no direct Ag...Ag interactions are present. In addition to the argentocyanide bridging, there

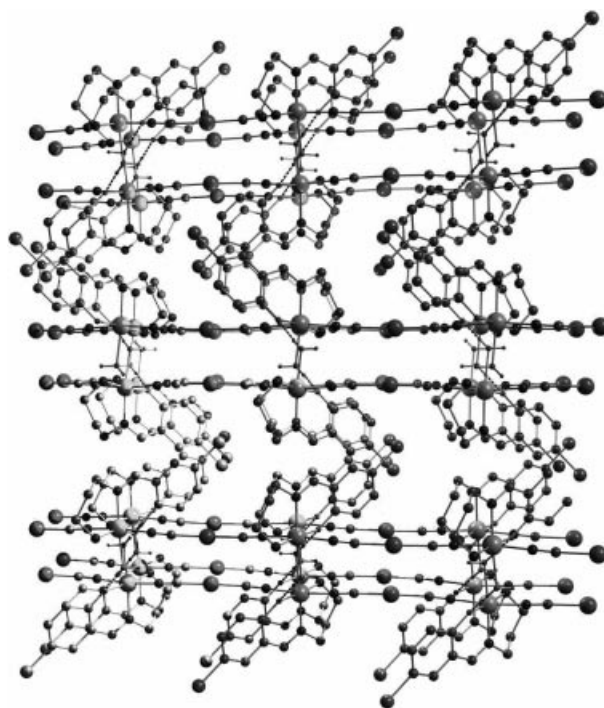


Figure 5. Packing diagram of complex **3**.

are intermolecular hydrogen-bonding interactions between the phenolate oxygen of the  $L^1$  moiety in one layer and the coordinated water oxygen of the next layer which form stable eight-membered rings [ $O2\cdots O1$  2.608(6) Å;  $\angle O2-H2O\cdots O1$  176(7)°] in an extended two-dimensional ladder-like network (Figure 6).

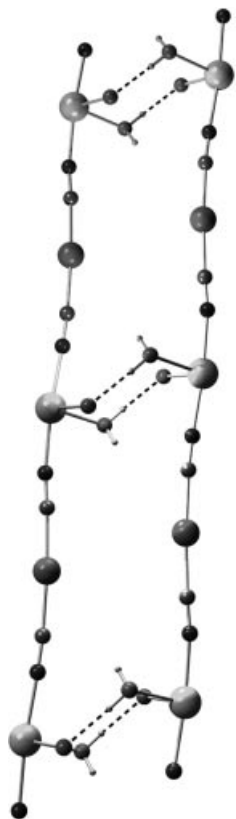


Figure 6. Packing fragment of complex 3 showing the ladder-like network.

### Structure of Complex 4

A perspective view of **4** together with the atom-labeling scheme is shown in Figure 7. Each nickel site is coordinated by two nitrogen atoms, a phenoxo oxygen atom of the tridentate  $L^2$  ligand, an oxygen atom of the methanol molecule, and two bridging nitrogen atoms of the  $[Ag(CN)_2]^-$  moiety. The average Ni–N bond length is 2.069 Å and the Ni–O<sub>phenolato</sub> and Ni–O<sub>methanol</sub> bond lengths are 2.0316(18) and 2.1135(19) Å, respectively. The N(O)–Ni–O(N) bond angles range from 86.77(9)° to 178.07(8)° (see Table 3), which means that the nickel centers display a distorted octahedral coordination geometry. The argentocyanide ion acts as a bridging ligand that connects the  $[NiL^3(MeOH)]^+$  moieties to form endless one-dimensional chains. The Ni $\cdots$ Ni separation within a chain is 10.414 Å, whereas the Ni $\cdots$ Ni separation between two successive chains is 5.052 Å. This distance is uniform throughout two successive layers. Moreover, adjacent chains are connected together through non-covalent interactions between the two coordinated phe-

nolato oxygen atoms (O1) in one layer and the methanol oxygen atom (O2) in the adjacent layer ( $O1\cdots O2$  2.586 Å) to form a 2D supramolecular network (Figure 8). It is noteworthy that this network adopts a wavelike layer (Figure 9) due to greater deviation of the bond angles [ $\angle Ni1-N3-C8$  166.4(2)° and  $\angle Ni1_a-N4-C9$  166.6(2)°] from planarity in the bridging argentocyanide moieties along the *b*-axis. The same bond angles in complex **3** are close to planarity, which means that the formation of a wavelike network can be ruled out and a chainlike network is obtained instead.

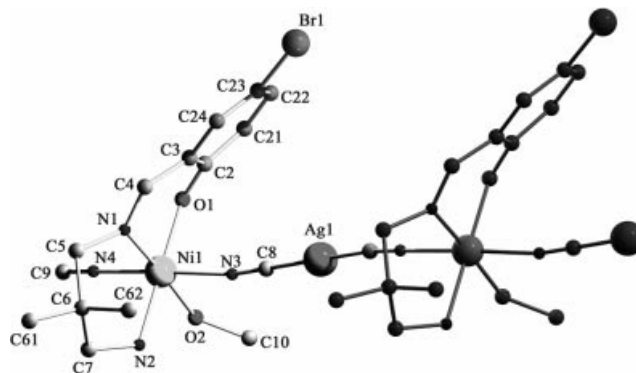


Figure 7. A view of the molecule of complex 4.

Table 3. Selected bond lengths [Å] and angles [°] in complex 4.

| Bond lengths [Å] |            |           |          |
|------------------|------------|-----------|----------|
| Ni1–O1           | 2.0316(18) | N3–C8     | 1.147(4) |
| Ni1–O2           | 2.1135(19) | Ag1–C8    | 2.050(3) |
| Ni1–N1           | 2.045(2)   | Ag1–C9    | 2.061(3) |
| Ni1–N2           | 2.088(3)   | N4–C9     | 1.142(4) |
| Ni1–N3           | 2.084(2)   |           |          |
| Bond angles [°]  |            |           |          |
| O1–Ni1–O2        | 95.50(9)   | O1–Ni1–N1 | 86.77(9) |
| O1–Ni1–N2        | 178.07(8)  | O1–Ni1–N3 | 89.69(9) |
| O2–Ni1–N1        | 177.40(9)  | O2–Ni1–N2 | 85.91(9) |
| O2–Ni1–N3        | 90.66(8)   | N1–Ni1–N2 | 91.86(9) |
| N1–Ni1–N3        | 90.61(9)   | N2–Ni1–N3 | 88.98(9) |
| C8–Ag1–C9        | 175.27(13) |           |          |

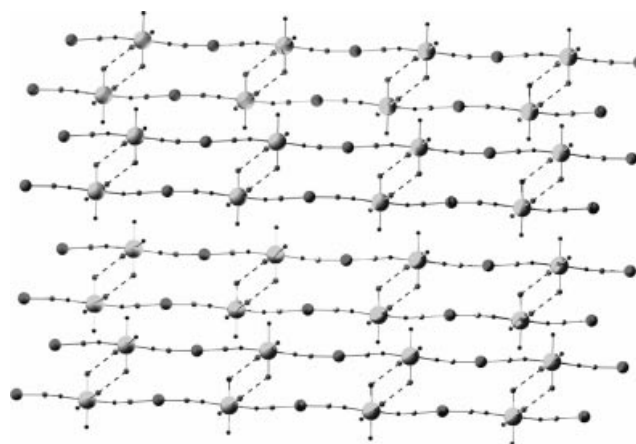


Figure 8. Packing diagram of complex 4.

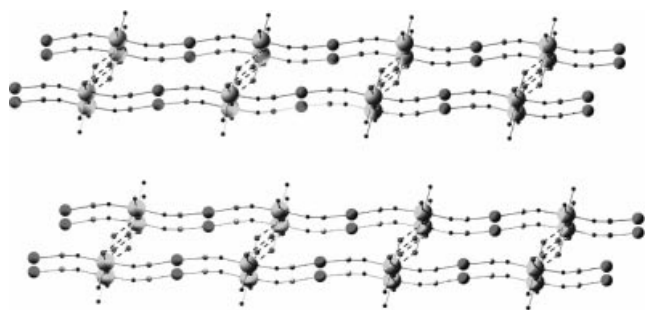


Figure 9. A view of the packing fragment of **4** showing the 2D wave-like network.

### Heterogeneous Catalysis

The use of nickel complexes with cyclam and salen ligands as active catalysts in the epoxidation of alkenes<sup>[17–22]</sup> has been reported in the literature. Some examples include the use of (salen)Ni-type complexes in faujasites for the oxidation of phenol with H<sub>2</sub>O<sub>2</sub>,<sup>[23]</sup> the epoxidation of cyclohexene and 1-hexene by NaOCl,<sup>[24,25]</sup> as well as the use of [Ni(salen)] immobilized on several solid supports as a catalyst for hydrogenation reactions.<sup>[26]</sup> More recently, Ferreira et al.<sup>[11]</sup> have carried out an extensive study of (salen)Ni<sup>II</sup> complexes as homogeneous catalysts and, after immobilization in zeolites (X and Y; following the “ship-in-a-bottle” procedure), as heterogeneous catalysts in the epoxidation of *trans*- $\beta$ -methylstyrene by NaOCl (considered to be environmentally more friendly).

The heterogeneous oxidation reactions were carried out using 1.0 g of substrate and 0.200 g of loaded catalyst (0.050 g of solid complex in the case of complex **2**) in 10 mL of CH<sub>3</sub>CN whilst stirring in a two-necked, round-bottomed flask fitted with a water condenser in an oil bath at 333 K. *tert*-Butyl hydroperoxide (equimolar with respect to the substrate) was added immediately before the start of the reaction. The products were collected from the reaction mixture after different time intervals and analyzed by gas chromatography. They were identified by comparison with known standards.

Tables 4, 5, and 6 show the results obtained with for the various Ni complexes immobilized on silica. Acetonitrile was used as the solvent in all cases. The major products of the reactions are epoxides and the selectivities for these compounds are very high. The very high TONs obtained for the oxidation of styrene,  $\alpha$ -methylstyrene, and cyclohexene suggest a very high catalytic efficiency for the nickel hydroperoxo species that could form in the presence of *tert*-butyl hydroperoxide. Small amounts of the corresponding diols were also obtained for all substrates.

Complex **2** is insoluble in all common solvents therefore instead of immobilizing it on mesoporous silica this pure complex was used as a solid catalyst. Our experimental results show that the TONs obtained with the immobilized catalysts are better than the pure nickel complex **2** for all the olefin substrates and that among these substrates cyclo-

Table 4. Epoxidation of styrene<sup>[a]</sup> catalyzed by complexes **1–4**.

| Entry | Catalyst | Conversion [%] <sup>[b]</sup> | Epoxide selectivity | TON <sup>[c]</sup> |
|-------|----------|-------------------------------|---------------------|--------------------|
| 1     | <b>1</b> | 39                            | 81                  | 121                |
| 2     | <b>2</b> | 56                            | 82                  | 36                 |
| 3     | <b>3</b> | 41                            | 91                  | 127                |
| 4     | <b>4</b> | 66                            | 83                  | 205                |

[a] Solvent: CH<sub>3</sub>CN; temperature: 333 K; complex **2** was used as a solid catalyst whereas the other catalysts were impregnated on a 2D hexagonal mesoporous silica. [b] Reaction time: 24 h; conversion and TON were measured by GC using *n*-decane as internal standard. [c] TON: mol of substrate converted per mole of Ni<sup>II</sup> present in catalyst used for the reaction.

Table 5. Epoxidation of  $\alpha$ -methylstyrene<sup>[a]</sup> catalyzed by complexes **1–4**.

| Entry | Catalyst | Conversion [%] <sup>[b]</sup> | Epoxide selectivity | TON <sup>[c]</sup> |
|-------|----------|-------------------------------|---------------------|--------------------|
| 1     | <b>1</b> | 56                            | 86                  | 153                |
| 2     | <b>2</b> | 76                            | 93                  | 43                 |
| 3     | <b>3</b> | 69                            | 78                  | 189                |
| 4     | <b>4</b> | 61                            | 89                  | 167                |

[a] Solvent: CH<sub>3</sub>CN; temperature: 333 K; complex **2** was used as a solid catalyst whereas the other catalysts were impregnated on a 2D hexagonal mesoporous silica. [b] Reaction time: 24 h; conversion and TON were measured by GC using *n*-decane as internal standard. [c] TON: mol of substrate converted per mole of Ni<sup>II</sup> present in catalyst used for the reaction.

Table 6. Epoxidation of cyclohexene<sup>[a]</sup> catalyzed by complexes **1–4**.

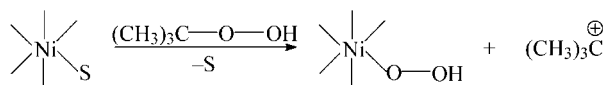
| Entry | Catalyst | Conversion [%] <sup>[b]</sup> | Epoxide selectivity | TON <sup>[c]</sup> |
|-------|----------|-------------------------------|---------------------|--------------------|
| 1     | <b>1</b> | 82                            | 82                  | 323                |
| 2     | <b>2</b> | 89                            | 82                  | 72                 |
| 3     | <b>3</b> | 81                            | 87                  | 319                |
| 4     | <b>4</b> | 89                            | 84                  | 350                |
| 5     | <b>4</b> | 87                            | 79                  |                    |
| 6     | <b>4</b> | 33                            | 29                  |                    |

[a] Solvent: CH<sub>3</sub>CN; temperature: 333 K; complex **2** was used as a solid catalyst whereas the other catalysts were impregnated on a 2D hexagonal mesoporous silica. [b] Reaction time: 24 h; conversion and TON were measured by GC using *n*-decane as internal standard. [c] TON: mol of substrate converted per mole of Ni<sup>II</sup> present in catalyst used for the reaction.

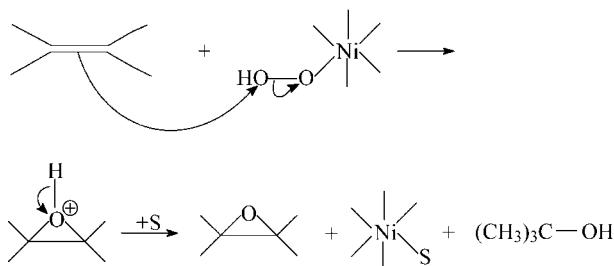
hexene shows the highest conversion and TON; the epoxide selectivities for styrene and  $\alpha$ -methylstyrene are also very good.

Microporous and mesoporous titanium silicates have been widely employed in the epoxidation of aromatic and alicyclic unsaturated compounds<sup>[27]</sup> in the presence of dilute aqueous H<sub>2</sub>O<sub>2</sub> as oxidant. The intermediate titanium hydroperoxo species formed play a crucial role in catalyzing the epoxidation reaction. The water molecules present in **1–3** and the methanol moiety in **4** could help the Ni complex to form such Ni hydroperoxide species in presence of H<sub>2</sub>O<sub>2</sub>, similar to the titanium silicate surface, and this could help in the catalysis of these epoxidation reactions (Scheme 3).

One control experiment was carried out for cyclohexene over immobilized catalyst **4** to check the efficiency of subsequent catalytic cycles and whether Ni leaches from these catalysts (Table 6, entry 4). After the initial experiment the catalyst was washed thoroughly with acetonitrile and then



S = solvent (H<sub>2</sub>O/MeOH)



Scheme 3. Proposed mechanism for the partial oxidation of styrene,  $\alpha$ -methylstyrene, and cyclohexene by *tert*-butyl hydroperoxide with complexes **1–4** as catalyst.

treated with 0.1 M HCl solution in EtOH for 8 h at 343 K and finally dried at 373 K for 2 h. It was then re-used as catalyst for a second experiment (Table 6, entry 5). The catalytic activity was found to remain practically the same, with only a marginal difference in the epoxide selectivity. This suggests that there is almost no Ni leaching into the liquid phase from these immobilized catalysts. A blank reaction of the oxidation of cyclohexene in the absence of any solid catalyst under otherwise identical reaction conditions was also carried out (Table 6, entry 6). The results show very poor conversion and epoxide selectivity in this case, thereby confirming the catalytic role of the Ni complex and the immobilized catalysts in these epoxidation reactions.

Figures 10, 11, and 12 show bar diagrams for the epoxidation of the alkenes over different immobilized catalysts at 333 K. It is clear from these figures that all the Ni<sup>II</sup> complexes act as efficient epoxidation catalysts in the presence of *tert*-butyl hydroperoxide as oxidant. Figure 13 shows the alkene conversion as a function of reaction time for the

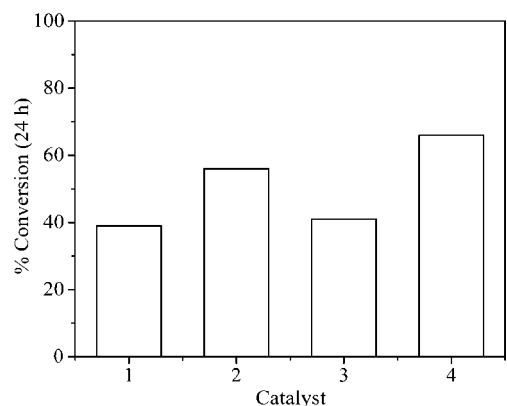


Figure 10. Bar diagram showing the catalytic activity of complexes **1–4** with styrene (CH<sub>3</sub>CN, 333 K).

epoxidation of styrene catalyzed by the four Ni<sup>II</sup> complexes. The conversions follow a sigmoid curve and reach maximum conversion after 24 h. It is apparent from these experimental observations that immobilized Ni complex **4** is most

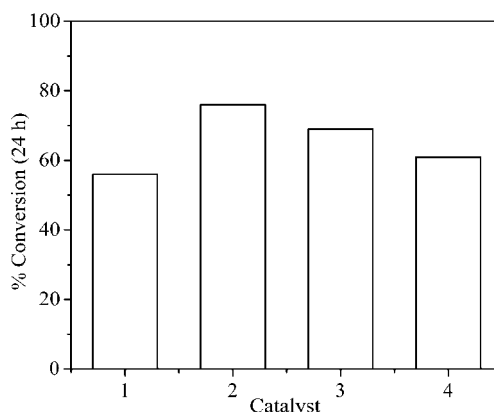


Figure 11. Bar diagram showing the catalytic activity of complexes **1–4** with  $\alpha$ -methylstyrene (CH<sub>3</sub>CN, 333 K).

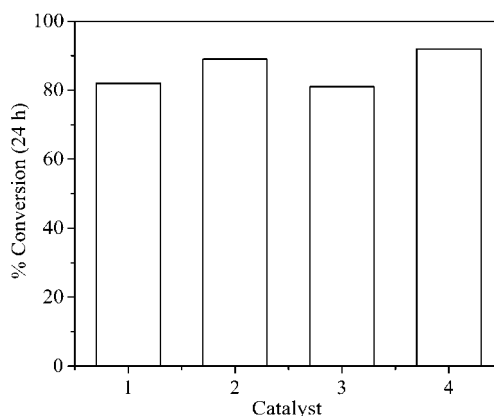


Figure 12. Bar diagram showing the catalytic activity of complexes **1–4** with cyclohexene (CH<sub>3</sub>CN, 333 K).

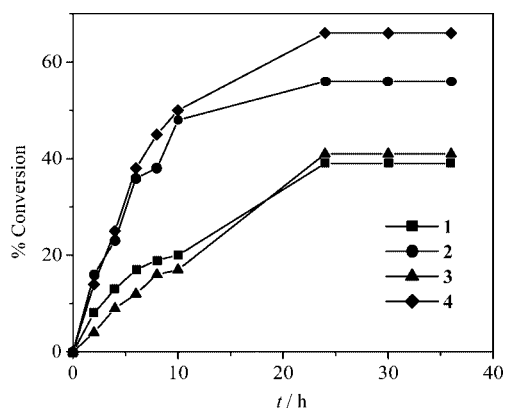


Figure 13. Conversion vs. time plot for the epoxidation of styrene with *tert*-butyl hydroperoxide catalyzed by complexes **1–4** (CH<sub>3</sub>CN, 333 K).

reactive for the epoxidation of all three substrates with high TONs (205, 167, and 350 for styrene,  $\alpha$ -methylstyrene, and cyclohexene, respectively).

### Magnetic Behavior of 1

The temperature dependencies of  $\chi_M T$  and  $\chi_M$  for complex **1** are plotted in Figure 14. The value of  $\chi_M T$  observed at room temperature (4.54 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K) is typical for four uncoupled Ni<sup>II</sup> ions with  $g > 2.00$ , as expected. On lowering the temperature the  $\chi_M T$  product decreases smoothly, reaching 0.05 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K. This behavior clearly points to the existence of moderate antiferromagnetic interactions between the Ni<sup>II</sup> centers, which result in a diamagnetic ground state. This is confirmed by the shape of the  $\chi_M$  vs.  $T$  curve, which passes through a maximum at around 22 K.

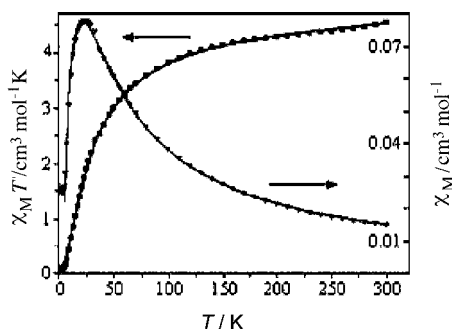


Figure 14. Temperature-dependence of  $\chi_M T$  (left scale, full squares) and  $\chi_M$  (right scale, full triangles) for **1** and best fit curves obtained with the parameters reported in the text. The theoretical curves calculated with the two different models cannot be discerned.

An initial quantitative analysis of the results obtained was performed using a simple isotropic Hamiltonian that considers all the possible exchange interactions in the tetramer [Equation (1)].

$$\hat{H} = J(S_1 S_2 + S_3 S_4) + J'(S_1 S_3 + S_1 S_4 + S_2 S_3 + S_2 S_4) + g\beta S H \quad (1)$$

where  $J$  is the exchange coupling within each dinuclear moiety, in other words the exchange interactions transmitted by the two phenolato bridges and the carboxylato one, and  $J'$  describes the coupling through the terephthalato bridging ligand. The fit was implemented using the CLUMAG package,<sup>[28]</sup> including a temperature-independent paramagnetism term ( $N_a = (8 \pm 2) \times 10^{-4}$  emu mol<sup>-1</sup>), which yields the best fit parameters  $J = 14.5 \pm 0.6$  cm<sup>-1</sup>,  $J' = 3.8 \pm 1.2$  cm<sup>-1</sup>, and  $g = 2.15 \pm 0.02$ . This set of parameters results in a diamagnetic ground state, as expected, with the first triplet lying 14.5 cm<sup>-1</sup> higher in energy. This is in fair agreement with the  $M$  vs.  $H$  curve (Figure 15), which shows the beginning of a singlet–triplet field induced transition at the highest measured field.

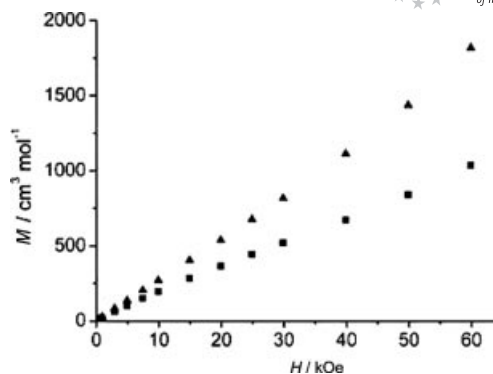


Figure 15.  $M$  vs.  $H$  curve for **1** measured at 2.7 (squares) and 5.1 K (triangles).

The obtained value of  $J'$  appears to be relatively large and higher than would be expected on the basis of literature data.<sup>[29]</sup> This might, in principle, be due to the neglecting of the single-ion zero-field-splitting terms that affect the shape of the calculated temperature dependence of the susceptibility curve in the same way as an intermolecular coupling.<sup>[30]</sup> We therefore fitted the data by including these terms using the Ginsberg formula for dinuclear Ni<sup>II</sup> centers with interdimer interactions.<sup>[30,31]</sup> The best fit parameters obtained with this approach were  $J = 14.5 \pm 0.2$  cm<sup>-1</sup>, in perfect agreement with the simple isotropic approach,  $2zJ' = 3.4 \pm 0.6$  cm<sup>-1</sup>,  $N_a = (4.5 \pm 2) \times 10^{-4}$  emu mol<sup>-1</sup>,  $g = 2.17 \pm 0.02$ , and  $D = 1\text{--}8$  cm<sup>-1</sup>, with the latter parameter having only a weak effect on the calculated curve. We can conclude on the basis of the two fits that the Ni–Ni interaction in each dinuclear moiety is close to 14.5 cm<sup>-1</sup> and that a non-negligible interaction is transmitted by the terephthalato ligand, in contrast to what is normally assumed.<sup>[32]</sup> The value of the Ni–Ni coupling constant in the dinuclear moiety is somewhat larger than would be expected on the basis of simple magnetostructural correlations derived for centrosymmetric bis(phenolato)-bridged dinuclear nickel complexes derived by Thompson's group<sup>[33]</sup> [Equation (2)].

$$J = +7.27\theta - 704.06 \quad (2)$$

where  $\theta$  is the bridging Ni–O–Ni angle. Using the average value of the bridging angle (96.94°) for  $\theta$  would result in a predicted value of  $J = 0.8$  cm<sup>-1</sup> for **1**, far from what is observed experimentally. We attribute this discrepancy to the effect of the carboxylato ligand, which bridges the two nickel ions in a *syn-syn* fashion and provides an additional pathway for the antiferromagnetic coupling between the two centers.<sup>[34]</sup> Finally, we note that the importance of the interdimer exchange coupling provided by the terephthalato ligand lies in the large  $\pi$ -connectivity it may provide, thus providing a relatively efficient pathway whilst keeping the interacting metal centers far apart.

### Conclusions

We have prepared four polymeric nickel(II)/Schiff-base complexes with terephthalate and argentocyanide as bridg-

ing moieties. Complex **1** is tetranuclear and its X-ray crystal structure shows that each tetranuclear unit contains both phenolate and terephthalate bridges. These tetranuclear units are connected together by the terephthalate units in a bis(monodentate) coordination mode to form an infinite 1D network. Variable-temperature magnetic measurements show that this complex exhibits moderate antiferromagnetic coupling. Complex **2** has the same structure as complex **1**, although we were unable to obtain crystals suitable for X-ray diffraction. Both complexes **3** and **4** form 2D polymeric networks utilizing the bridging argentocyanide units and strong noncovalent interactions.

Alkene epoxidation studies have been performed with all the complexes as active heterogeneous catalysts. Styrene,  $\alpha$ -methylstyrene, and cyclohexene are all efficiently converted into their corresponding epoxides. The experimental results show that immobilized Ni complex **4** is the most active catalyst for the epoxidation of all three substrates (TON values of 205, 167, and 350 for styrene,  $\alpha$ -methylstyrene, and cyclohexene, respectively).

## Experimental Section

**Starting Materials:** Salicylaldehyde, 5-bromosalicylaldehyde, 1,3-diaminopropane, 1,3-diamino-2,2-dimethylpropane, terephthalic acid, and Ni<sup>II</sup> salts were purchased from commercial sources and used as received. Sodium terephthalate was readily prepared by the reaction of terephthalic acid with a stoichiometric amount of NaOH in water. All other chemicals (sodium hydroxide, AgNO<sub>3</sub>, and NaCN) were of reagent grade. Ethanol, methanol, and dmf were of reagent grade and used without further purification. Doubly distilled water was used throughout. The acetonitrile used in the epoxidation reaction was of HPLC grade. *tert*-Butyl hydroperoxide purchased from Aldrich was used as oxidant. The substrates styrene,  $\alpha$ -methylstyrene, and cyclohexene were also obtained from Aldrich.

**Physical Measurements:** Microanalyses (CHN) were performed with a Perkin–Elmer 240C elemental analyzer. FT-IR spectra were obtained on a Nicolet, MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. A Perkin–Elmer 2380 AAS was used for wet chemical analysis. GC analysis was carried out with an Agilent Technologies 6890N network GC system equipped with a fused silica capillary column (30 m  $\times$  0.32 mm) and a FID detector. The column temperature was increased from 80 °C (4 min) to 220 °C at a rate of 5 °C min<sup>-1</sup>. The injection temperature was 200 °C. The solid-state electronic spectra were measured with a Shimadzu UV 2401PC spectrophotometer using a BaSO<sub>4</sub> pellet as background standard. Magnetic measurements were performed with a Cryogenic SQUID S600 magnetometer operating between 2 and 300 K with applied magnetic fields of up to 65 kOe. Raw data were corrected for diamagnetic contribution of the sample holder and the intrinsic diamagnetism of the sample estimated by Pascal's constants.

**General Procedure for the Preparation of the Immobilized Catalysts:** For the synthesis of the mesoporous silica,<sup>[35]</sup> the cationic surfactant cetyl trimethylammonium bromide (2.96 g) was mixed with an aqueous solution containing sodium dodecyl sulfate (0.47 g) and vigorously stirred at room temperature for 30 min. Gel formation occurred immediately leading to a viscous suspension. Tetraethyl orthosilicate (3.5 g) was added to this suspension with continuous

stirring for 30 min. After 2 h constant stirring, tetraethylammonium hydroxide was added dropwise until the color of the solution turned white. The pH value of the final mixture was about 11.0. The resultant mixture was aged overnight whilst stirring at room temperature and then transferred into a polypropylene bottle and heated at 80 °C for 72 h without stirring. The solid produced was recovered by filtration, washed several times with water, and dried at room temperature. The resulting powder was calcined at 703 K to remove the organic surfactants. The molar ratio of the various constituents was TEOS/CTAB/SDS/H<sub>2</sub>O = 50:25:5:4500. For loading of the Ni<sup>II</sup> complexes, 1.0 g of the calcined solid was suspended in 50 mL of dmf containing 0.2 g of complex. The mixture was stirred for 4 h at room temperature, then filtered off and washed several times with dmf and dried in vacuo at ambient temperature. The loading (immobilization) of the Ni complexes on the mesoporous host was confirmed by UV/Vis solid state spectroscopy.

**Bis(3-aminopropyl-5-bromosalicylideneiminato)nickel(II) [Ni(L<sup>1</sup>)<sub>2</sub>]:** This complex was prepared following the method of Elder.<sup>[36]</sup> Thus, a solution of 1,3-diaminopropane (8.88 g, 120 mmol) in ethanol was heated at 60 °C and a solution of 5-bromosalicylaldehyde (4.02 g, 20 mmol) in ethanol added dropwise with stirring for 30 min. After the addition was complete, solid Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (2.49 g, 10 mmol) was added at once. The solid dissolved rapidly to give a dark solution, which was refluxed for 20 min at 60 °C. The green precipitate that formed was filtered off, washed with a small amount of ethanol and diethyl ether, and dried in air.

**Bis(3-aminopropylsalicylideneiminato)nickel(II) [Ni(L<sup>2</sup>)<sub>2</sub>]:** This complex was also prepared by the method described by Elder.<sup>[36]</sup>

**Bis(3-aminopropyl-5-bromo-2,2-dimethylsalicylideneiminato)nickel(II) [Ni(L<sup>3</sup>)<sub>2</sub>]:** This complex was prepared in a similar manner to Ni(L<sup>1</sup>)<sub>2</sub>. Thus, a solution of 1,3-diamino-2,2-dimethylpropane (6.13 g, 60 mmol) in ethanol was heated at 60 °C and a solution of 5-bromosalicylaldehyde (2.01 g, 10 mmol) in ethanol was added dropwise with stirring for 30 min. The deep yellow precipitate obtained dissolved after the addition of solid Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (1.25 g, 5 mmol) at once. The solid dissolved rapidly to give a dark brown solution, which was refluxed for 30 min at 60 °C. The green precipitate obtained was filtered off, washed with a small amount of ethanol and diethyl ether, and dried in air.

**[Ni<sub>4</sub>L<sup>1</sup><sub>4</sub>( $\mu$ -tp- $\kappa$ -O)(H<sub>2</sub>O)<sub>2</sub>( $\mu$ -tp- $\kappa$ -O)]·2C<sub>2</sub>H<sub>5</sub>OH·CH<sub>3</sub>OH·3H<sub>2</sub>O (**1**):** A solution of [Ni(L<sup>1</sup>)<sub>2</sub>] (0.057 g, 0.1 mmol) in 10 mL of hot ethanol was added to a methanolic solution (5 mL) of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.036 g, 0.1 mmol) with constant stirring. The color of the solution turned deep green. An aqueous solution of Na<sub>2</sub>tp (0.021 g, 0.1 mmol) was then added to this mixture. The resulting solution was stirred for 30 min, then filtered. Slow evaporation at room temperature yielded green crystals of **1** suitable for X-ray analysis after 4 d. Yield: 0.040 g (45%). C<sub>61</sub>H<sub>82</sub>Br<sub>4</sub>N<sub>8</sub>Ni<sub>4</sub>O<sub>20</sub> (1800.8): calcd. C 40.65, H 4.55, N 6.22; found C 39.40, H 4.70, N 6.40.

**[Ni<sub>4</sub>L<sup>2</sup><sub>4</sub>( $\mu$ -tp- $\kappa$ -O)(H<sub>2</sub>O)<sub>2</sub>( $\mu$ -tp- $\kappa$ -O)]·3H<sub>2</sub>O (**2**):** A solution of [Ni(L<sup>2</sup>)<sub>2</sub>] (0.083 g, 0.2 mmol) in 10 mL of hot ethanol was added to a methanolic solution (5 mL) of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.073 g, 0.2 mmol) with constant stirring. The color of the solution turned deep green. An aqueous solution of Na<sub>2</sub>tp (0.042 g, 0.2 mmol) was then added to this mixture. The resulting solution was stirred for 30 min, then filtered. This solution yielded dark green crystals of **2** on standing at room temperature for 3 d. Unfortunately, it was not possible to grow single crystals of X-ray diffraction quality. Yield: 0.085 g (63%). C<sub>56</sub>H<sub>70</sub>N<sub>8</sub>Ni<sub>4</sub>O<sub>17</sub> (1360.8): calcd. C 49.38, H 5.14, N 8.23; found C 49.29, H 5.06, N 8.17.

Table 7. Crystal data and details for structure refinement for **1**, **3**, and **4**.

|                                                       | <b>1</b>                                                                                          | <b>3</b>                                                            | <b>4</b>                                                            |
|-------------------------------------------------------|---------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------|
| Formula                                               | C <sub>122</sub> H <sub>160</sub> Br <sub>8</sub> N <sub>16</sub> Ni <sub>8</sub> O <sub>40</sub> | C <sub>12</sub> H <sub>14</sub> AgBrN <sub>4</sub> NiO <sub>2</sub> | C <sub>15</sub> H <sub>19</sub> AgBrN <sub>4</sub> NiO <sub>2</sub> |
| Formula weight                                        | 3599.62                                                                                           | 492.76                                                              | 533.83                                                              |
| Crystal system                                        | monoclinic                                                                                        | monoclinic                                                          | triclinic                                                           |
| Space group                                           | <i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)                                                       | <i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)                         | <i>P</i> 1̄ (no. 2)                                                 |
| <i>a</i> [Å]                                          | 12.073(2)                                                                                         | 10.204(2)                                                           | 8.2964(3)                                                           |
| <i>b</i> [Å]                                          | 18.601(4)                                                                                         | 21.706(4)                                                           | 10.4145(5)                                                          |
| <i>c</i> [Å]                                          | 16.998(3)                                                                                         | 8.0562(16)                                                          | 11.3805(5)                                                          |
| <i>a</i> / <i>b</i> / <i>c</i> [°]                    | 90/99.70(3)/90                                                                                    | 90/110.33(3)/90                                                     | 96.918(4)/102.963(4)/96.348(4)                                      |
| <i>V</i> [Å <sup>3</sup> ]                            | 3762.7(13)                                                                                        | 1673.2(6)                                                           | 941.60(7)                                                           |
| <i>Z</i>                                              | 1                                                                                                 | 4                                                                   | 2                                                                   |
| <i>D</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]       | 1.553                                                                                             | 1.956                                                               | 1.883                                                               |
| <i>μ</i> [mm <sup>-1</sup> ]                          | 3.180                                                                                             | 4.691                                                               | 4.175                                                               |
| <i>F</i> (000)                                        | 1764                                                                                              | 960                                                                 | 526                                                                 |
| Temperature [K]                                       | 294                                                                                               | 294                                                                 | 108                                                                 |
| <i>λ</i> [Å]                                          | 0.71073 (Mo- <i>K</i> <sub>α</sub> )                                                              | 0.71073 (Mo- <i>K</i> <sub>α</sub> )                                | 0.71073 (Mo- <i>K</i> <sub>α</sub> )                                |
| <i>θ</i> <sub>min</sub> – <i>θ</i> <sub>max</sub> [°] | 2.2–25.0                                                                                          | 2.1–30.0                                                            | 3.4–27.6                                                            |
| Reflections collected                                 | 6266                                                                                              | 5787                                                                | 9565                                                                |
| Independent reflections                               | 6093                                                                                              | 4857                                                                | 4287                                                                |
| Observed data [ <i>I</i> > 2σ( <i>I</i> )]            | 3140                                                                                              | 2516                                                                | 3373                                                                |
| Data/restraints/parameters                            | 6093/0/429                                                                                        | 4857/2/196                                                          | 4287/0/220                                                          |
| Goodness-of-fit on <i>F</i> <sup>2</sup>              | 0.889                                                                                             | 0.922                                                               | 0.927                                                               |
| Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]   | <i>R</i> <sub>1</sub> = 0.0828<br><i>wR</i> <sub>2</sub> = 0.1480                                 | <i>R</i> <sub>1</sub> = 0.0566<br><i>wR</i> <sub>2</sub> = 0.1145   | <i>R</i> <sub>1</sub> = 0.0286<br><i>wR</i> <sub>2</sub> = 0.0635   |
| <i>R</i> indices (all data)                           | <i>R</i> <sub>1</sub> = 0.2370<br><i>wR</i> <sub>2</sub> = 0.1872                                 | <i>R</i> <sub>1</sub> = 0.1145<br><i>wR</i> <sub>2</sub> = 0.1324   | <i>R</i> <sub>1</sub> = 0.0392<br><i>wR</i> <sub>2</sub> = 0.0656   |

**[Ni(L<sup>1</sup>)(H<sub>2</sub>O){Ag(CN)<sub>2</sub>}]<sub>n</sub> (**3**):** A methanolic solution (5 mL) of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.036 g, 0.1 mmol) was added to a methanolic solution (10 mL) of [Ni(L<sup>1</sup>)<sub>2</sub>] (0.057 g, 0.1 mmol) and the resulting green solution stirred for 10 min. An aqueous solution (5 mL) of Na[Ag(CN)<sub>2</sub>] (0.018 g, 0.1 mmol) was then added to this mixture and the solution stirred for 20 min. The solution was filtered to remove any suspended material and kept at room temperature. Slow evaporation of solvents yielded deep green crystals suitable for X-ray analysis after 7 d. Yield: 0.018 g (73%). C<sub>12</sub>H<sub>14</sub>AgBrN<sub>4</sub>NiO<sub>2</sub> (492.76): calcd. C 29.22, H 2.84, N 11.36; found C 29.16, H 2.79, N 11.23.

**[Ni(L<sup>3</sup>)(MeOH){Ag(CN)<sub>2</sub>}]<sub>n</sub> (**4**):** A methanolic solution (5 mL) of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.036 g, 0.1 mmol) was added to a methanolic solution (10 mL) of [Ni(L<sup>3</sup>)<sub>2</sub>] (0.057 g, 0.1 mmol) and the resulting green solution stirred for 10 min. A dmf solution (5 mL) of Na[Ag(CN)<sub>2</sub>] (0.018 g, 0.1 mmol) was then added to this mixture and the solution stirred for 20 min. It was then filtered and kept at room temperature. Slow evaporation of the solvents yielded green crystals suitable for X-ray analysis after 5 d. Yield: 0.021 g (40%). C<sub>15</sub>H<sub>20</sub>AgBrN<sub>4</sub>NiO<sub>2</sub> (534.83): calcd. C 33.66, H 3.74, N 10.47; found C 33.59, H 3.70, N 10.41.

**Crystal-Structure Determination:** Single crystals of complex **1** were grown from EtOH/MeOH/H<sub>2</sub>O and those of complexes **3** and **4** were grown from MeOH/H<sub>2</sub>O and dmf/MeOH medium, respectively. The X-ray single-crystal data for complexes **1** and **3** were collected with a Siemens P4 four-circle diffractometer whereas those of complex **4** were collected on an Oxford Instruments Sapphire2-CCD diffractometer. Crystal size: 0.18 × 0.21 × 0.51, 0.30 × 0.31 × 0.52, and 0.08 × 0.17 × 0.22 mm<sup>3</sup> for complexes **1**, **3**, and **4** respectively. Unit cell dimensions and intensity data were measured at 294 K for **1** and **3** and 108 K for **4**. The crystallographic data, conditions used for the intensity data collection and some features of the structure refinement are listed in Table 7. Graphite-monochromated Mo-*K*<sub>α</sub> radiation (*λ* = 0.71073 Å) was used to collect the data sets. Accurate unit-cell parameters for **1**, **3**,

and **4** were determined from automatic centering of 14, 15, and 5214 reflections, respectively, and refined by least-square methods. 6266 Reflections were collected for **1** in the range 2.2° < *θ* < 25.0°, 5787 reflections were collected in the range 2.1° < *θ* < 30.0° for **3**, and 7224 reflections were collected in the range 3.4° < *θ* < 27.6° for **4**. A total of 3140, 2516, and 3373 reflections were assumed as observed [*I* > 2σ(*I*)] for complexes **1**, **3**, and **4** respectively. All calculations for data reduction, structure solution and refinement were performed using standard procedures with SHELXS-97<sup>[37]</sup> and SHELXL-97.<sup>[38]</sup> All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on *F*<sup>2</sup>. The H atoms were constrained to idealized positions and refined isotropically using a riding model.

CCDC- 645841 (for **1**), -645842 (for **3**), and -645843 (for **4**) 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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