

Synthesis and Molecular Structures of Nickel(II) and Cobalt(III) Complexes with 2-(Arylimino)-3-(hydroxyimino)butane

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We report new series of Ni^{II} and Co^{III} complexes with nitrogen-donor chelating ligands of the (*E,E*)-2-(arylimino)-3-(hydroxyimino)butane type (Ar–N⁺N–OH). These ligands are characterized by a hydrophilic (OH group) and a hydrophobic region (aryl group). Ni^{II} derivatives were obtained either as trimers of formula [Ni₃(Ar–N⁺N–OH)₃Br₄(OH)][Br], with the hydrophobic groups oriented on the same side, or as bis(chelated) derivatives with *cis* geometry, depending on the steric hindrance of the aryl groups. Co^{III} complexes were obtained only as bis(chelated) derivatives, with the two li-

gands coplanar. The “*iso-oriented*” arrangement of ligands in bis(chelated) Co^{III} complexes is favored by weak interactions between the two ligands, namely O–H...O hydrogen bond and stacking interactions between the aryl groups. Co^{III} complexes might find application as catalysts for *living* or *controlled* radical polymerization of polar olefins, and preliminary results are reported.

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Introduction

Recent studies report that the molecular weights of polymers synthesized from olefin monomers with the aid of transition-metal catalysts or promoters can be tuned by the steric hindrance of the ancillary ligands.^[1–6] In particular, the steric properties can be modulated by the introduction of 2- or 2,6-substituted aryl groups in planar bi-, tri- and tetradentate nitrogen-donor chelates. Some notable examples are reported in Figure 1.

When the substituted aryl groups are arranged perpendicular to the plane of the chelate, they create a particular steric hindrance above and below the plane of the chelate itself (Figure 1). Bi- and tridentate ligands of variable steric hindrance are easily accessible thanks to the synthetic procedure based on the condensation reaction between biacetyl (or 2,6-diacetylpyridine) and an appropriate aromatic amine.^[1,2] On the other hand, convenient modulation of the steric hindrance is more difficult to achieve for tetradentate N-donor chelating ligands such as porphyrins or bis(dimethylglyoximate) derivatives.

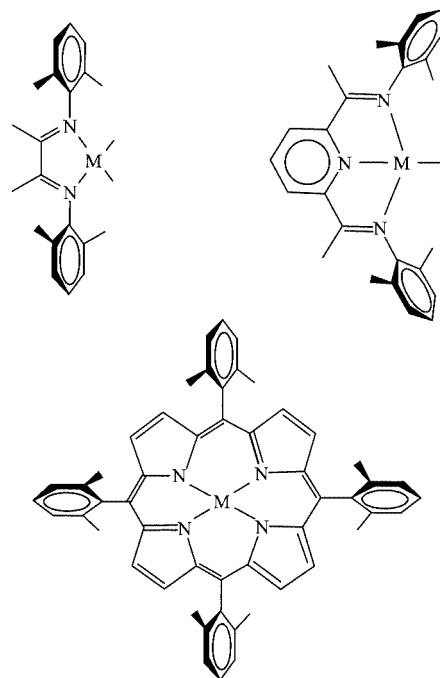


Figure 1. Examples of bi-, tri-, and tetradentate nitrogen-donor ligands and of the corresponding complexes

Such nitrogen-donor chelating ligands are of particular interest in the field of homogeneous catalysis. Depending on the nature of the metal, the olefin, and the experimental conditions, different reactions can be performed: nickel

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complexes with bidentate chelating ligands or cobalt and iron complexes with tridentate chelating ligands, in the presence of MAO, promote the oligomerization or polymerization of ethylene or propylene by a coordinative mechanism.^[1–5] Moreover, cobalt complexes with planar tetradentate chelating ligands have successfully been used in oligomerization and polymerization of polar olefins by a radical mechanism in the presence of AIBN [2,2'-azobis(isobutyronitrile)].^[6–10] In particular, organometallic Co^{III} complexes with planar sterically hindered N-donor tetradentate chelating ligands polymerize polar olefins by a *living* radical mechanism.^[6] In the absence of steric bulk, these complexes promote the oligomerization of the same substrates, yielding oligomers characterized by terminal C=C double bonds.^[7] Cobalt derivatives with dimethylglyoxime (cobaloximes)^[9] and analogous complexes, in which the bridging H atom is replaced by a BF₂ group,^[10] turned out to be very efficient and cheap oligomerization catalysts. The presence of two OH...O bridging moieties in cobaloxime derivatives ensures coplanarity of the two molecules of ligand, which is necessary for these complexes to show catalytic activity.^[7]

Interestingly, the effect of steric hindrance induced by chelating ligands is the same regardless of the type of polymerization mechanism. In both cases the chain termination step, a β -H elimination process, proceeding either through a coordinative^[1] or a radical mechanism,^[9,11,12] is slowed down with increasing bulkiness of the aryl moiety.

Very recently we reported that complexes of type *cis*-[Co(CH₂Ph)₂(N–N)₂][PF₆] (N–N = bipy, phen) promote acrylonitrile polymerization by a *controlled* radical mechanism,^[13] with behavior intermediate between that exhibited by cobalt complexes with sterically hindered and nonhindered planar tetradentate N-donor chelating ligands.

In this study we report the synthesis and characterization of nickel and cobalt complexes with a series of bidentate N-donor chelating ligands: namely, (*E,E*)-2-(arylimino)-3-(hydroxyimino)butanes (Ar–N⁺N–OH) (Figure 2, a). The ligands in which the aryl group is phenyl or *o*-tolyl, are known^[14,15] and the series has now been extended to other substituted amines.

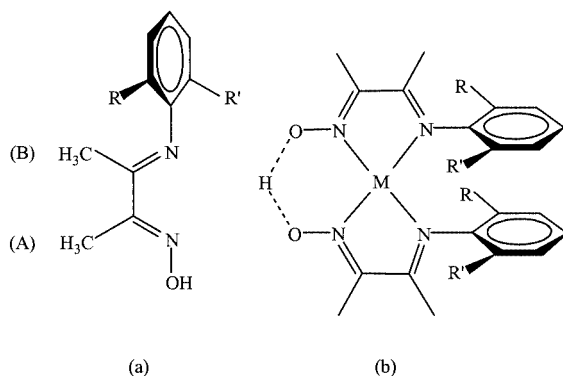


Figure 2. (a) Generic 2-(arylimino)-3-(hydroxyimino)butane ligand (Ar–N⁺N–OH); (b) corresponding bis(chelated) planar complex

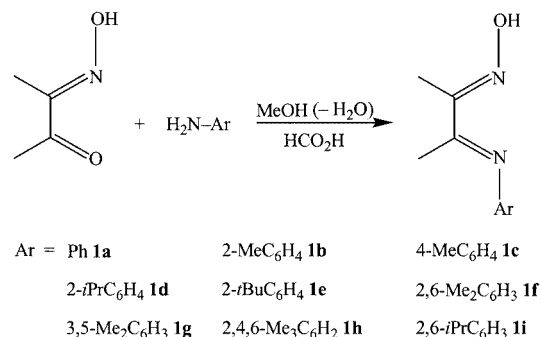
These ligands are characterized by a hydrophilic (OH) and a hydrophobic region (Ar). Therefore, with a ligand/metal ratio of 2:1, the formation of planar bis(chelated) species can be predicted, thanks to the possibility of establishing weak interactions between the two molecules of Ar–N⁺N–OH, such as the hydrogen bond between the oxygen atoms and/or the stacking interaction between the aromatic rings (Figure 2, b). Unlike that in the planar bis(dimethylglyoxime) derivatives, the steric bulk in these complexes is directed normally to the equatorial plane and can be modulated by varying the nature of substituents in the 2- and the 6-positions of the aromatic ring.

Some results on the catalytic activity of the cobalt derivatives in the polymerization of methyl methacrylate (MMA) are also presented.

Results and Discussion

Synthesis and Characterization of 2-(Arylimino)-3-(hydroxyimino)butane Ligands 1a–1i

The chelating ligands (*E,E*)-2-(arylimino)-3-(hydroxyimino)butane are obtained by condensation of biacetyl monoxime with a series of different substituted aromatic amines (Scheme 1).



Scheme 1. Synthesis of Ar–N⁺N–OH ligands 1a–1i

Syntheses were conducted in methanol at reflux for 5 h, starting from stoichiometric amounts of reagents, and in the presence of formic acid in catalytic amount. All ligands were obtained in high yields as white, crystalline solids. Crystals of **1h** suitable for X-ray diffraction analysis were obtained upon slow cooling of the reaction mixture.

Its structural characterization, with regard to the two N=C double bonds, shows a *syn*-methyl,*syn*-methyl conformation (Figure 3) that would require a rotation about the C(2)–C(3) bond in order to behave as a chelating ligand. The planarity of the O–N=C–C=N fragment, with a torsion angle of 162.7(5)°, is indicative of π -electron delocalization in the heterodiene fragment, as confirmed by the C(2)–C(3) bond length of 1.462(6) Å. This in fact appears to be slightly shorter than the accepted value of 1.48 Å for a C(sp²)–C(sp²) single bond.^[16] It may be of interest to point out the difference between the C=N–C angles at the N(2) imino and the N(1) oxime nitrogen atoms [120.1(5) and 111.8(4)°, respectively]. The mesitylene ring is roughly

perpendicular to the planar residue of the molecule, making a dihedral angle of 73° , an arrangement induced by steric hindrance between the groups. The crystal packing consists of chains with a zigzag motif, running along the crystallographic c axis, where $\text{O}(1)\text{--H}\cdots\text{N}(2)$ hydrogen bonds [$\text{O}\cdots\text{N} = 2.749(5)$ Å] connect adjacent molecules. The molecular geometry and the packing resemble those found in the p -tolyl analogue.^[15]

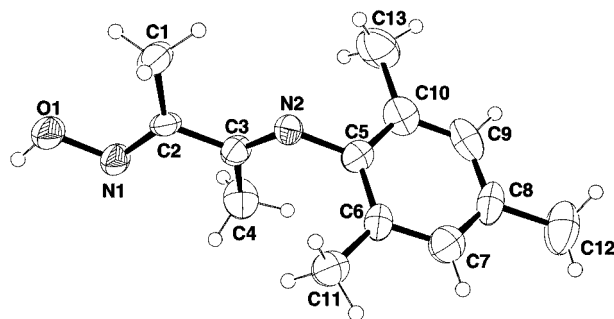
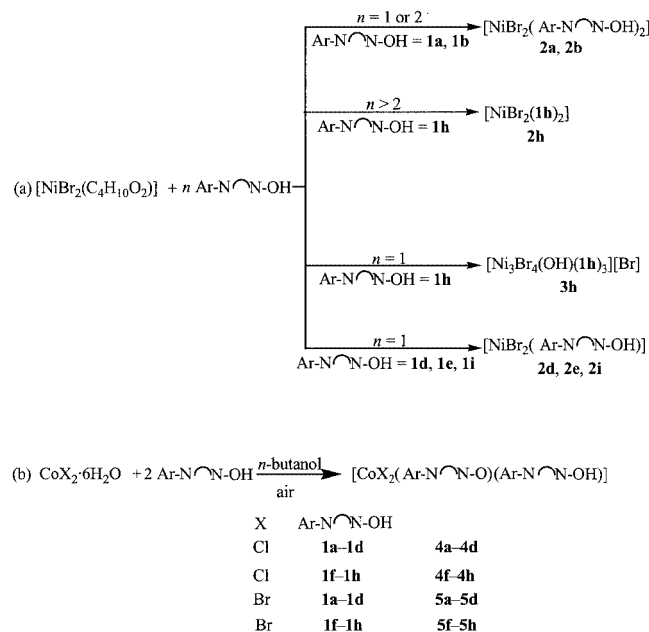


Figure 3. Molecular structure of ligand **1h** (ORTEP drawing, thermal ellipsoids 40% probability); selected bond lengths [Å] and angles [$^\circ$]: $\text{O}(1)\text{--N}(1)$ 1.395(4), $\text{N}(1)\text{--C}(2)$ 1.283(5), $\text{N}(2)\text{--C}(3)$ 1.269(5), $\text{N}(2)\text{--C}(5)$ 1.434(6), $\text{C}(1)\text{--C}(2)$ 1.487(5), $\text{C}(2)\text{--C}(3)$ 1.462(6), $\text{C}(3)\text{--C}(4)$ 1.493(5); $\text{C}(2)\text{--N}(1)\text{--O}(1)$ 111.8(4), $\text{C}(3)\text{--N}(2)\text{--C}(5)$ 120.1(5).

The ligands have been characterized by ^1H NMR spectroscopy in CDCl_3 (Table 1). ^1H NMR spectra exhibit two characteristic regions: aromatic (protons of the aryl groups at $\delta \approx 6\text{--}7.5$ ppm) and aliphatic (methyl groups of the biacetyl monoxime backbone and aromatic ring substituents at $\delta \approx 2\text{--}3$ ppm). A broad peak belonging to the OH group is also visible between $\delta \approx 7.80$ and 8.40 ppm. The assignment of signals to protons was based on NOE and COSY experiments. The signal of methyl group (A) in all the ligands was further downfield than that of the methyl group (B) (Figure 2, a); for the aryl protons, a downfield shift is observed on going from the β to the γ and to the α protons. The latter trend was also observed for alkyl substituents on the aromatic ring. These chelating ligands were used for the synthesis of both Ni^{II} and Co^{III} complexes.

Synthesis and Characterization of the Ni^{II} Complexes **2a**, **2b**, **2d**, **2e**, **2h**, **2i**; **3h**

Synthesis of complexes was carried out in CH_2Cl_2 , at room temperature, for 3 h, starting from $[\text{NiBr}_2(\text{C}_4\text{H}_{10}\text{O}_2)]$ ($\text{C}_4\text{H}_{10}\text{O}_2$ = ethylene glycol dimethyl ether) and using a ligand/nickel ratio of 1:1 or 2:1 (Scheme 2, a). The products were isolated as brown solids upon addition of diethyl ether or n -pentane to the reaction mixture.



Scheme 2. Synthesis of (a) nickel and (b) cobalt complexes

The products of the reaction were characterized by elemental analyses (Table 2) and, depending on the nature of the ligand, complexes of different stoichiometry were obtained. In particular, when ligands of low steric hindrance, such as **1a** and **1b**, were used, the products were bis(chelated) complexes of formula $[\text{NiBr}_2(\text{Ar-N}\text{---}\text{N-OH})_2]$ (**2a**, **2b**), regardless of the ligand/nickel ratio used in the synthesis. With the more hindered ligands **1d**, **1e**, and **1i**, a monochelated species was obtained when the synthesis was carried out with a ligand/nickel ratio of 1:1 (**2d**, **2e**, **2i**). No

Table 1. ^1H NMR spectroscopic data for ligands **1a–1i**

Ligand ^[a]	CH_3 (A)	CH_3 (B)	OH	H^α	$\text{H}^{\alpha'}$	H^β	$\text{H}^{\beta'}$	H^γ
1a	2.20 (s)	2.01 (s)	8.25 (t)	6.72 (d)	6.72 (d)	7.30	7.30	7.09 (t)
1b	2.23 (s)	2.05 (s)	8.19 (s)	1.94 (s)	6.56 (d)	7.16–7.20 (m)	7.16–7.20 (m)	7.00 (t)
1c	2.18 (s)	2.00 (s)	n.d.	6.62 (d)	6.62 (d)	7.12 (d)	7.12 (d)	2.33 (s)
1d	2.24 (s)	1.99 (s)	7.85 (s)	1.15 (d), 2.88 (m)	6.51 (d)	7.29 (d)	7.05–7.17 (m)	7.05–7.17 (m)
1e	2.26 (s)	2.01 (s)	8.39 (s)	1.30 (s)	6.40 (d)	7.39 (d)	7.15 (t)	7.05 (t)
1f	2.25 (s)	1.84 (s)	7.90 (s)	1.96 (s)	7.03 (d)	7.03 (d)	6.91 (t)	
1g	2.18 (s)	2.00 (s)	7.90 (s)	6.34 (s)	6.34 (s)	2.30 (s)	2.30 (s)	6.72 (s)
1h	2.25 (s)	1.83 (s)	8.14 (s)	1.93 (s)	1.93 (s)	6.85 (s)	6.85 (s)	2.22 (s)
1i	2.27 (s)	1.87 (s)	8.34 (s)	1.13 (d), 2.58–2.65 (m)	1.13 (d), 2.58–2.65 (m)	7.05–7.15 (m)	7.05–7.15 (m)	

[a] Spectra recorded in CDCl_3 , at room temperature; δ , ppm; s = singlet, d = doublet, t = triplet, m = multiplet; n.d. = not determined; the signals of the protons of the alkyl substituents on the aryl group are reported in the place of the corresponding protons.

Table 2. Elemental analyses for the nickel complexes **2a**, **2b**, **2d**, **2e**, **2h**, **2i** and **3h** and the cobalt complexes **4a–4d**, **4f–4h**, **5a–5d**, **5f–5h**

Ni complexes (yield)	C ^[a]	H ^[a]	N ^[a]
2a (53%)	41.30 (42.10)	4.13 (4.10)	9.66 (9.81)
2b (51%)	42.90 (44.11)	4.63 (4.71)	9.23 (9.35)
2d ^[b] (57%)	35.20 (37.54)	4.39 (4.44)	6.34 (6.74)
2e ^[b] (44%)	36.80 (37.29)	4.49 (4.47)	6.01 (6.34)
2h (60%)	48.80 (47.67)	5.87 (5.53)	8.83 (8.55)
2i ^[b] (53%)	40.80 (40.13)	5.26 (5.05)	5.60 (5.84)
3h (52%)	38.80 (40.10)	4.65 (4.70)	6.87 (7.20)
Co complexes (yield)	C ^[a]	H ^[a]	N ^[a]
4a (71%)	49.20 (49.91)	4.71 (4.81)	11.50 (11.64)
5a (83%)	42.10 (42.13)	4.00 (4.06)	9.84 (9.82)
4b (75%)	51.10 (51.88)	5.28 (5.34)	11.00 (11.00)
5b (76%)	44.20 (44.10)	4.58 (4.71)	9.39 (9.35)
4c (80%)	51.70 (51.88)	5.35 (5.34)	11.00 (11.00)
5c (78%)	44.10 (44.10)	4.51 (4.71)	9.41 (9.35)
4d (82%)	54.90 (55.23)	6.25 (6.24)	9.81 (9.91)
5d (80%)	47.72 (47.72)	5.39 (5.39)	8.59 (8.56)
4f (72%)	53.30 (53.64)	5.78 (5.81)	10.20 (10.24)
5f (74%)	45.50 (45.95)	4.90 (5.14)	8.77 (8.93)
4g (74%)	53.60 (53.64)	5.80 (5.81)	10.40 (10.42)
5g (80%)	46.30 (45.95)	5.03 (5.14)	9.01 (8.93)
4h (73%)	55.40 (55.23)	6.29 (6.24)	9.93 (9.91)
5h (73%)	46.80 (47.72)	5.36 (5.39)	8.36 (8.56)

^[a] Calculated values in parentheses. ^[b] The yield was calculated by formulating the complex as [NiBr₂(Ar–N[∘]N–OH)].

bis(chelated) species was isolated when a ligand/nickel ratio > 1:1 was used. For the ligand with the mesityl group, **1h**, the bis(chelated) derivative [NiBr₂(**1h**)₂] (**2h**) was the product when the synthesis was performed with an excess of ligand. On the other hand, a monochelated species was obtained when a ligand/nickel ratio of 1:1 was used.

Single crystals suitable for X-ray analysis were obtained for the complexes with ligands **1a** (Figure 4) and **1h** (Figure 5), by slow precipitation from a dichloromethane solution with diethyl ether.

The structural determination of complex **2a** confirms its formulation as a bis(chelated) species with the nickel atom in a distorted octahedral coordination geometry. The two bromide ions are in a *cis* arrangement and the two *cis* chelating ligands **1a** are bound to the metal atom in a *head-to-tail* configuration with a dihedral angle of 85.8(4)° (Figure 4). The Ni–N coordination bond lengths involving oxime nitrogen donors *trans* to bromide are longer than the Ni–N(1) and Ni–N(3) bonds *trans* to each other by about 0.08 Å. The Ni–Br bond lengths of 2.561(2) Å are between the values found for the bridging Br[−] in **3h** (see below). The N(2)–Ni–Br(1) and N(4)–Ni–Br(2) bond angles of about 165.5° deviate significantly from those expected for a regular octahedron. Nevertheless, each oxime hydrogen atom is pointing, at about 2.5 Å, toward the halide ion and the values for the bond angles could give support to an OH⋯Br interaction.

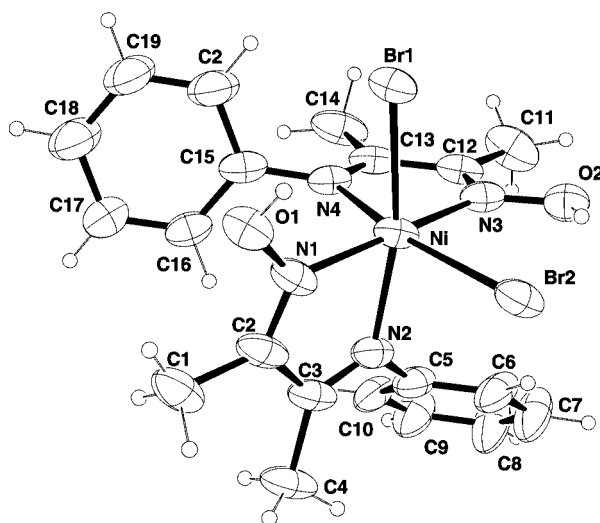


Figure 4. Molecular structure of compound **2a** (ORTEP drawing, thermal ellipsoids 40% probability); selected bond lengths [Å] and angles [°]: Ni–N(1) 2.026(8), Ni–N(2) 2.109(7), Ni–N(3) 2.018(8), Ni–N(4) 2.094(8), Ni–Br(1) 2.561(1), Ni–Br(2) 2.561(2); N(1)–Ni–N(2) 76.4(3), N(3)–Ni–N(4) 75.8(3), N(1)–Ni–N(3) 172.5(3), N(2)–Ni–Br(1) 166.1(3), N(4)–Ni–Br(2) 165.0(2), Br(1)–Ni–Br(2) 93.38(5).

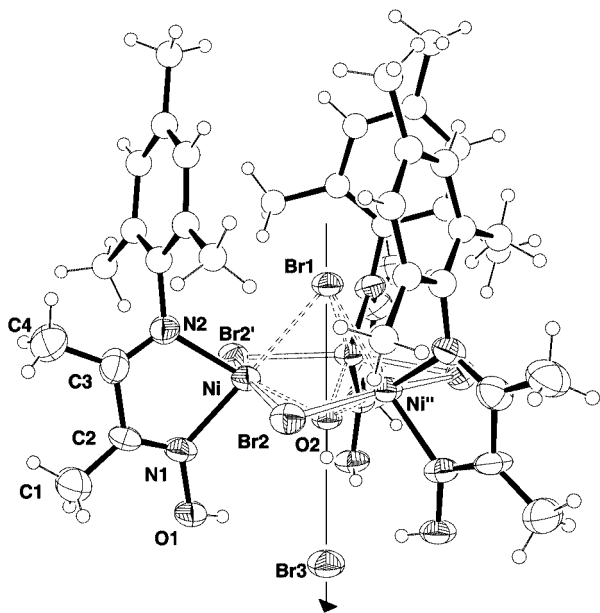


Figure 5. Molecular structure of compound **3h**; for sake of clarity aryl C atoms are indicated as spheres of fixed radius; selected bond lengths [Å] and angles [°]: Ni–Ni' 3.026(2), Ni–Br(1) 2.598(2), Ni–Br(2') 2.551(2), Ni–Br(2) 2.578(2), Ni–O(2) 1.999(5), Ni–N(1) 2.024(8), Ni–N(2) 2.051(8); N(1)–Ni–N(2) 78.6(4), O(2)–Ni–N(1) 105.9(4), O(2)–Ni–N(2) 175.5(4), O(2)–Ni–Br(1) 76.8(3), O(2)–Ni–Br(2) 82.02(5), O(2)–Ni–Br(2') 82.73(5), N(1)–Ni–Br(1) 175.4(3), N(2)–Ni–Br(1) 98.8(2), Br(2)–Ni–Br(2') 164.67(7), Ni–Br(1)–Ni' 71.24(6), Ni–Br(2)–Ni'' 72.32(6), Ni–O(2)–Ni'' 98.4(3); symmetry codes: (') $-x + y + 1, -x + 1, z$; (') $-y + 1, x - y, z$.

The X-ray analysis of the complex with ligand **1h** reveals that it is a trinuclear species, corresponding to the formulation [Ni₃Br₄(OH)(**1h**)₃][Br] (**3h**).

The unique and unexpected structure of complex **3h** is shown in Figure 5, together with selected bond lengths and angles. Its C_3 symmetry is illustrated by the view along the symmetry axis (Figure 6). The metal ions of three monochelated Ni(**1h**) fragments form an equilateral triangle. On each edge, the pair of nickel atoms, separated by 3.026(2) Å, is μ_2 -bridged by a bromide ligand, slightly displaced by 0.2 Å from the Ni_3 plane, with Ni–Br(2) bond lengths of 2.551(2) and 2.578(2) Å. Another bromide ion and a hydroxy oxygen atom μ_3 -bridge all the nickel ions with coordination distances of 2.578(2) and 1.999(5) Å, respectively. These capping species lie on the threefold axis, above [Br(1) +1.923(2) Å] and below [O(2) –0.97(1) Å] the metal plane. The coordination geometry around each nickel atom thus involves the nitrogen-donor atoms of a chelating ligand **1h**, three bromide ions, and a hydroxy group with bond angles that considerably deviate from the ideal octahedral values.

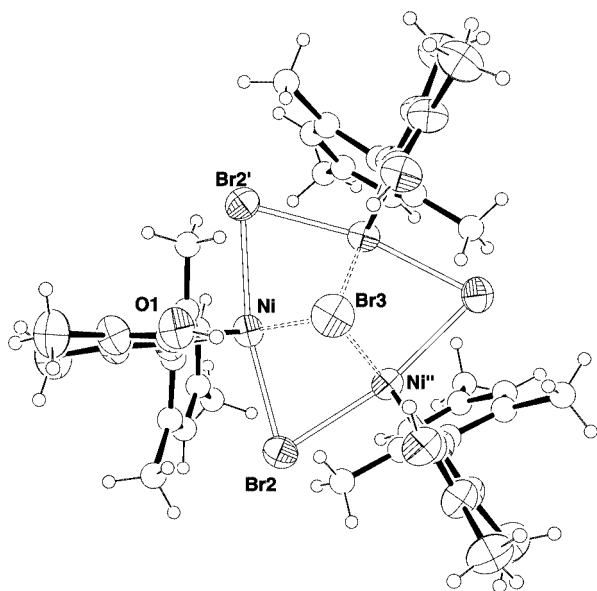


Figure 6. Projection down the threefold axis of the molecular structure of **3h**

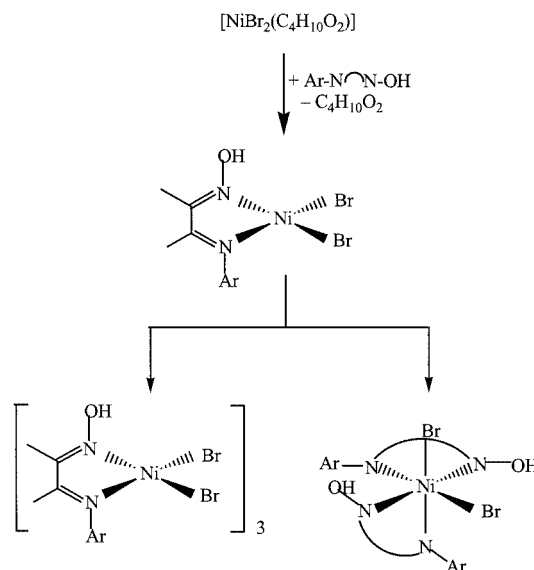
In the ligand, the C(2)–C(3) bond length of 1.522(14) Å, although of low accuracy, agrees with a single bond character indicating that, upon coordination, the delocalization inside the O–N=C–C=N moiety of the ligand seems to be removed.

To the best of our knowledge, two structures containing a strictly analogous Ni_3X_3 core ($X = \text{halide}$)^[17,18] and with metal atoms capped by an oxygen atom and another halide ion have been reported; their Ni–Ni distances, averaged to 3.05 Å, are closely similar to those here. One of these, with tetramethylethylenediamine as chelating ligand (L) and with chloride replacing the bromide anions, has the same stoichiometry $[Ni_3X_4(OH)L_3][X]$.^[17a] A trimeric copper species $[Cu_3(ClO_4)(OH)L'_3]^+$ containing the deprotonated ligand **1a** (L') has also been reported.^[17b] However, the crystal structure shows that L' behaves as a tridentate species: it chelates a metal ion with the N atoms and simultaneously

binds a close copper unit through the O donor, becoming almost coplanar with the metal triangle.

It is worth noting that in the current compound the electronic structural features of ligand **1h** give rise to an assembly possessing well-defined hydrophobic and hydrophilic domains. The former is delimited by the mesitylene groups. The aromatic rings, inclined to form an angle of 80.7(3)° with the Ni_3 plane, enclose the μ_3 -bridging Br(1). The hydrophilic area is confined at the oxime groups side, where a bromide ion is displaced by an hydroxy oxygen μ_3 -bridge. The bromide ion, Br(3), is settled on the threefold axis and accounts for the neutral charge of the whole compound. The latter anion is located at 3.236(10) Å from the oxime oxygen atoms O(1) and at 3.322(7) Å from O(2), probably interacting with the hydrogen atoms of the hydroxy groups (Figure 5).

On the basis of these results, a reaction mechanism is proposed for the formation of the different synthetic products (Scheme 3).



Scheme 3. Proposed mechanism for the synthesis of nickel complexes

The reaction proceeds by initial formation of the monochelated monomeric species, which, depending on the steric hindrance of the ligand, can then evolve along different pathways. For ligands of low steric hindrance (**1a**, **1b**), the reaction moves rapidly towards the formation of bis(chelated) complexes, even at low ligand/Ni ratios. For the mesityl derivative, with ligand/Ni = 1:1, the monochelated derivative is isolated as the trimer **3h**, while with an excess of ligand the bis(chelated) species **2h** is the product. With the sterically more hindered ligands **1d**, **1e** and **1i**, only the formation of monochelated species of unknown nuclearity is observed.

Synthesis and Characterization of Co^{III} Complexes **4a–4d**, **4f–4h**, **5a–5d**, **5f–5h**

Synthesis was carried out in the presence of air, in *n*-butanol, at room temperature, for 3 h, starting from

$\text{CoX}_2 \cdot n\text{H}_2\text{O}$ salts ($\text{X} = \text{Cl}, \text{Br}$) and using a ligand/cobalt ratio of 1:1 or 2:1 (Scheme 2, b). In all cases, the formation of a red solid is observed immediately after addition of the ligands, followed by its transformation in the final product into a green microcrystalline solid. A total of 14 complexes (chloro and bromo derivatives) have been synthesized. However, the synthesis of **4a** and **5a** derivatives was reported several years ago.^[14]

On the basis of elemental analyses (Table 2), all the complexes were formulated as $[\text{CoX}_2(\text{Ar}-\text{N}^{\text{O}}\text{N}-\text{O})-(\text{Ar}-\text{N}^{\text{O}}\text{N}-\text{OH})]$ [$\text{X} = \text{Cl}$ (**4**), Br (**5**)]. Therefore, in contrast to the nickel derivatives, only octahedral bis(chelated) species are obtained with all the ligands tested, regardless of the ligand/cobalt ratio used.

Single crystals suitable for X-ray analysis were obtained for **5b** and **5h** by crystallization from $\text{CH}_2\text{Cl}_2/n$ -pentane. Figures 7 and 8 (ORTEP drawings, thermal ellipsoids at 50% probability) give perspective views of the molecular structures of compounds **5b** and **5h**, the latter being located on a crystallographic twofold axis passing through the metal atom and in the middle between the oxime oxygen atoms. Unlike in the nickel derivatives, the two bromide ions are in a *trans* arrangement, so the chelating ligands define the equatorial plane of the molecule. Moreover, they are bound to the cobalt atom in a *head-to-head* configuration, in contrast to the *head-to-tail* arrangement proposed for **4a** and **5a** on the basis of steric considerations.^[14] The Co–Br and Co–N coordination bond lengths have comparable values in the two complexes. In contrast, the values of the Br–Co–Br bond angles, probably affected by steric hindrance between the bromide ions and the proximal

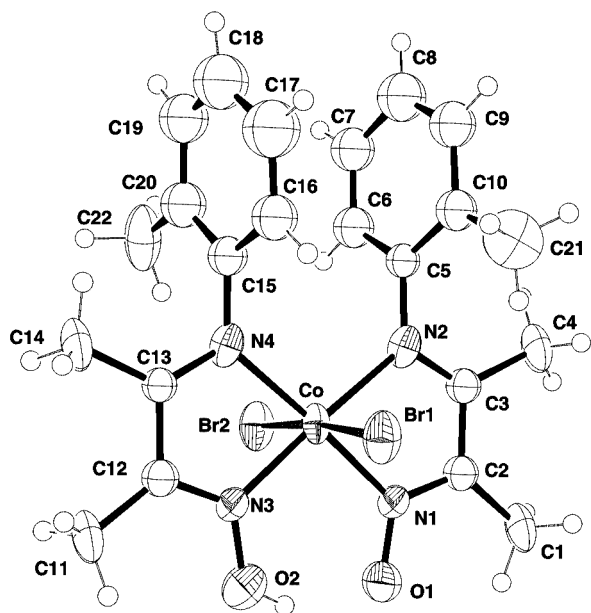


Figure 7. Molecular structure of compound **5b**; selected coordination bond lengths [Å] and angles [°]: Co–Br(1) 2.389(2), Co–Br(2) 2.385(2), Co–N(1) 1.895(11), Co–N(2) 2.006(11), Co–N(3) 1.906(11), Co–N(4) 1.997(11); N(1)–Co–N(2) 80.6(3), N(1)–Co–N(3) 96.2(5), N(1)–Co–N(4) 176.3(5), N(2)–Co–N(3) 176.7(5), N(2)–Co–N(4) 103.1(5), N(3)–Co–N(4) 80.1(3), Br(1)–Co–Br(2) 174.12(13)

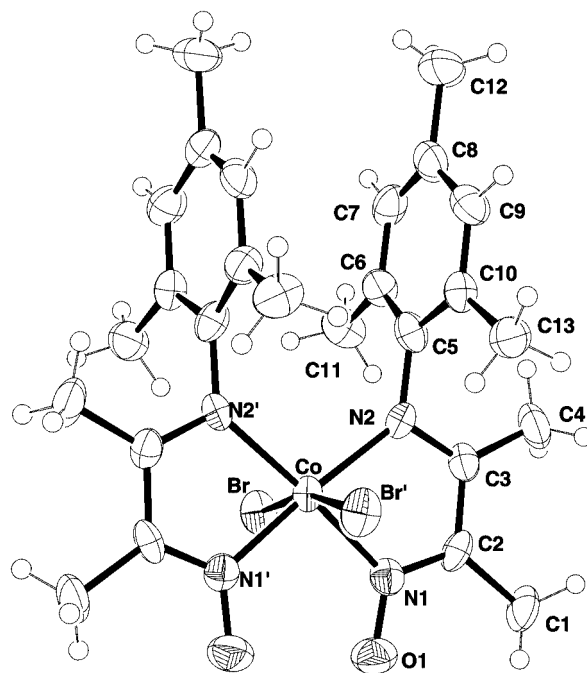


Figure 8. Molecular structure of compound **5h** with atom labelling scheme of the crystallographically independent moiety; selected bond lengths [Å] and angles [°]: Co–Br 2.386(1), Co–N(1) 1.912(6), Co–N(2) 2.006(6), N(1')–Co–N(1) 95.2(3), N(1)–Co–N(2) 80.7(2), N(1)–Co–N(2') 175.9(2), N(2)–Co–N(2') 103.5(3), N(1')–Co–Br 85.1(2), N(1)–Co–Br 85.3(2), N(2)–Co–Br 94.4(2), N(2')–Co–Br 94.4(2), Br–Co–Br' 165.64(7); primed atoms at $-x + 1, -y + 1, z$

methyl groups on the phenyl rings, are 174.1(1) and 165.64(7)° in the *o*-tolyl and in the mesityl derivative, respectively. The atoms of the five-membered rings are close to coplanar and the calculated angles of 1.6 (**5b**) and 5.4° (**5h**) represent a slight tilting between the chelating ligand moieties.

The *head-to-head* arrangement of the mixed Schiff-base/oxime ligands favors the formation of an $\text{OH} \cdots \text{O}$ bridge. The mean $\text{O} \cdots \text{O}$ distance for the two structures of 2.42(1) Å is shorter than those found in the widely studied $[\text{Co}(\text{DH})_2]$ and $[\text{Co}(\text{DO})(\text{DOH})(\text{pn})]$ complexes^[19] [mean values of 2.487(2) and 2.45(1) Å,^[20] respectively]. It was suggested that the $\text{O} \cdots \text{O}$ distance should parallel the ease of deprotonation, as indicated by the slower exchange of the proton in $(\text{DO})(\text{DOH})\text{pn}$ than in $(\text{DH})_2$ complexes of similar axial ligands.^[21,22] The formation of the H-bridge in **5h** causes a remarkable shortening of the N–O [1.288(7) Å] and of the N(oxime)=C [1.292(9) Å] bonds with respect to those detected in the free ligand, and the same trend is also observed for **5b**, although the values found here are less accurate.

Moreover, the aromatic rings, with an orientation similar to that found in the uncoordinated ligand, ensure intramolecular π -stacking. In fact, the interplanar angle formed by the facing *o*-tolyl rings in **5b** is 15.0(3)° and the C $\cdots$ C distances between the *ipso*-carbon atoms and the carbon atoms in *para* positions are 3.35 and 3.84 Å, respectively. It is worth noting that the dihedral angle between the aryl

groups in **5h** is reduced to 5.5(3)°, and that the C...C separations are correspondingly somewhat shorter (3.18 and 3.76 Å, respectively), indicating a closer approach and hence a more efficient π -interaction between the bulky mesitylene groups.

Therefore, the *head-to-head* arrangement of the chelating ligands gives rise to an H-bridge and to an aryl π -stacking that act as a double clamp providing additional stability to the complexes. The geometrical data for the cobalt compounds reported here are quite comparable, but a detailed analysis shows that the steric effects around the metal center can be modulated by changing the nature of the aryl substituents.

These complexes were characterized in solution by recording NMR spectra in CDCl₃ at room temperature (Table 3). The signal of the methyl group (A) bound to the carbon atom closest to the oxime nitrogen atom is the most shifted (almost 0.40 ppm downfield shift) with respect to the signals of the free ligand. No signal due to the hydroxy group is visible in the spectra of the complexes. It can be seen that the spectrum of complexes with the *o*-tolyl-substituted ligand presents two sets of signals of different intensity both for the alkyl and aryl protons, thus indicating the presence of two species in solution. At room temperature the signals are quite broad. An NOE was observed between the methyl group of *o*-tolyl and H α' and H β . On the other hand, when the signals of the methyl groups (A and B) of the skeleton were irradiated in different NOE experiments, no NOE was seen, other than that expected between the two signals themselves. These results suggest that the two species in solution correspond to two rotamers, differing in the relative orientations of the methyl group of the *o*-tolyl substituents: namely *syn* and *anti* isomers. The broadness of the signals suggests that the two rotamers are in equilibrium and the rate of this equilibrium is slow on the NMR timescale.

The Co^{III} complex with ligand **1g**, [Co(Cl)₂{**1g**-(H)}(**1g**)], was treated with NaBH₄ in methanol in the presence of

CH₃I, to yield a red, microcrystalline solid. The elemental analysis confirms the ratio Co/**1g** = 1:2 and is in agreement with the formation of the organometallic derivative [Co(CH₃)(I){**1g**-(H)}(**1g**)] (**6g**). The ¹H NMR spectrum, recorded in CDCl₃ at room temperature, shows three singlets of the same intensity in the region of the aromatic protons, and five singlets for the methyl groups, one of which is of half intensity with respect to the other four peaks. This last is therefore attributed to the methyl group bound to the cobalt atom. The other assignments of signals to protons were based on comparison with the spectrum of the starting complex **4g**. In particular, the groups in the α - and β -positions of the aromatic rings generate two different signals, thus indicating the lack of the equatorial plane of the complex as a plane of symmetry. The Co–CH₃ and Co–I bonds are therefore in a *trans* configuration. Finally, it is reasonable to assume that the two N[⌢]N ligands are bound to the cobalt atom in the *head-to-head* arrangement, as in the starting complex. This behavior is analogous to that typical of the dimethylglyoxime and (DO)(DOH)pn derivatives.^[23]

Polymerization of Methyl Methacrylate

Some preliminary test polymerizations of methyl methacrylate were performed with complex **5b** by carrying out the reaction in the presence of AIBN as initiator, in THF as solvent. The result is compared with the activity of the system based on AIBN itself (Table 4).

Table 4. Polymerization of methyl methacrylate

Promoter ^[a]	Yield [g]	Mw	Mw/Mn
AIBN	2.34	420 000	1.7
AIBN + 5b ^[b]	5.59	83 300	1.4

^[a] Reaction conditions: $n_{\text{AIBN}} = 2.9 \cdot 10^{-2}$ mmol; solvent THF $V = 11$ mL; MMA $V = 12$ mL; $T = 60$ °C; $t = 5$ h. ^[b] [AIBN]/[Co] = 15.

Table 3. ¹H NMR spectroscopic data for cobalt complexes **4a–4d**, **4f–4h**, **5a–5d**, **5f–5h**

Complexes ^[a]	CH ₃ (A)	CH ₃ (B)	H α	H α'	H β	H β'	H γ
4a	2.67 (s)	2.05 (s)	6.77 (d)	6.77 (d)	6.91 (t)	6.91 (t)	7.10 (t)
5a	2.66 (s)	2.07 (s)	6.85–6.92 (m)	6.85–6.92 (m)	6.85–6.92 (m)	6.85–6.92 (m)	7.08 (t)
4b	2.67 (s)	2.04 (s)	1.96 (s)	6.64 (d)	6.90–7.00 (m)	7.28 (dd)	6.90–7.00 (m)
5b	2.68 (s)	2.06 (s)	2.04 (s)	6.65 (d)	6.85–7.00 (m)	7.48 (d)	6.85–7.00 (m)
4c	2.65 (s)	2.06 (s)	6.64–6.71 (m)	6.64–6.71 (m)	6.64–6.71 (m)	6.64–6.71 (m)	2.30 (s)
5c	2.65 (s)	2.08 (s)	6.70–6.74 (m)	6.70–6.74 (m)	6.70–6.74 (m)	6.70–6.74 (m)	2.30 (s)
4d	2.67 (s)	2.10 (s)	1.10 (d), 1.28 (d) 2.90 (m)	6.75 (dd)	6.42 (t)	7.13 (dd)	7.04 (t)
5d	2.69 (s)	2.12 (s)	1.12 (d), 1.32 (d) 2.97 (m)	6.97 (dd)	6.41 (t)	7.13 (d)	7.02 (t)
4f	2.70 (s)	2.06 (s)	2.03 (s)	2.03 (s)	6.64 (d)	6.64 (d)	6.86 (t)
5f	2.72 (s)	2.08 (s)	2.10 (s)	2.10 (s)	6.64 (d)	6.64 (d)	6.86 (t)
4g	2.65 (s)	2.05 (s)	6.44 (s)	6.44 (s)	2.16 (s)	2.16 (s)	6.71 (s)
5g	2.64 (s)	2.07 (s)	6.53 (s)	6.53 (s)	2.16 (s)	2.16 (s)	6.70 (s)
4h	2.69 (s)	2.07 (s)	1.99 (s)	1.99 (s)	6.47 (s)	6.47 (s)	2.21 (s)
5h	2.71 (s)	2.09 (s)	2.06 (s)	2.06 (s)	6.48 (s)	6.48 (s)	2.23 (s)

^[a] Spectra recorded in CDCl₃, at room temperature; δ [ppm]; s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet; n.d. = not determined; the signals of the protons of the alkyl substituents on the aryl group are reported in the place of the corresponding protons.

The addition of the complex, even if in low amount with respect to AIBN, resulted in a doubling of the yield of polymerization and, at the same time, in a fivefold decrease in the molecular weight together with a decrease in polydispersity. These complexes therefore show a behavior typical of chain-transfer catalysts (CCTCs).^[7]

Conclusion

The coordination chemistry of the new N-ligands towards Ni^{II} and Co^{III} has been studied, different behavior being observed depending both on the ligand and on the metal. In the case of Ni^{II}, when unhindered ligands were used, octahedral bis(chelated) species were obtained, while the product with more hindered ligands was a monochelated trimer. In this last compound the three molecules of chelating ligands are "iso-oriented", producing one hydrophilic and one hydrophobic hole. In the case of Co^{III}, octahedral bis(chelated) species are obtained with all the ligands used. Their main structural feature is the presence of weak interactions between the two coplanar N-ligands, namely O–H...O hydrogen bond and stacking interactions between the aryl groups.

These bis(chelated) Co^{III} complexes have several similarities to the well-known cobaloximes^[7] and to (DO)-(DOH)pn derivatives,^[24] previously studied by us and further investigated by Finke.^[25,26] As reported in the introduction, these complexes are efficient chain transfer catalysts, and give oligomers in high yield for methyl methacrylate and styrene. The new complexes reported here could behave very similarly but, thanks to the variable steric hindrance, could give polymers instead of oligomers. The molecular mass of the polymers should increase on increasing the steric bulk of the N-ligands. The study of their catalytic behavior and the characterization of polymers is currently under investigation.

Experimental Section

Materials and Instrumentation: Chemicals and solvents were obtained from commercial sources (Aldrich, Carlo–Erba) and were used as received. NMR spectra were recorded with a Jeol EX 400 spectrometer operating at 400.0 MHz for ¹H. ¹H chemical shifts were measured relative to the residual solvent peak versus TMS (CDCl₃ at δ = 7.26 ppm and CD₂Cl₂ at δ = 5.33 ppm for ¹H). Two-dimensional correlation spectra (COSY) were obtained with the automatic program of the instrument. NOE experiments were run with a ¹H pulse of 90° and 12.5 μ s. THF was dried with metallic sodium. MMA used in the polymerization reactions was purified by extraction with a water solution of NaOH and distilled.

Synthesis of Ligands: (*E,E*)-2-(Hydroxyimino)-3-(phenylimino)butane (**1a**), (*E,E*)-2-(hydroxyimino)-3-(*o*-tolylimino)butane (**1b**), (*E,E*)-2-(hydroxyimino)-3-(*p*-tolylimino)butane (**1c**), (*E,E*)-2-(hydroxyimino)-3-[(2-isopropylphenyl)imino]butane (**1d**), (*E,E*)-2-[(2-*tert*-butylphenyl)imino]-3-(hydroxyimino)butane (**1e**), (*E,E*)-2-[(2,6-dimethylphenyl)imino]-3-(hydroxyimino)butane (**1f**), (*E,E*)-2-

[(3,5-dimethylphenyl)imino]-3-(hydroxyimino)butane (**1g**), (*E,E*)-2-(hydroxyimino)-3-[(2,4,6-trimethylphenyl)imino]butane (**1h**), (*E,E*)-2-[(2,6-diisopropylphenyl)imino]-3-(hydroxyimino)butane (**1i**). These ligands were synthesized by heating a solution of biacetyl monoxime (0.02 mol) and the stoichiometric amount of amine at reflux in methanol (5 mL) in the presence of formic acid (3 drops) as catalyst for 4–5 h. Ligands **1a**, **1b**, **1c**, and **1d** were obtained by cooling the solutions at 4 °C for 2–3 h after reflux. White crystals were filtered off, washed with ether, and dried in vacuo. Ligand **1d** was recrystallized from *n*-pentane. Ligands **1e**, **1f**, **1g**, **1h**, and **1i** were obtained by cooling the solutions at room temp after reflux. Ligand **1i** precipitated from the heated solution after 1.5 h reaction time. Crystalline precipitates were filtered, washed with ether, and dried in vacuo. All ligands are colorless, with the exception of **1e**, which precipitated as a yellow solid. The values of elemental analyses are reported in Table 5.

Table 5. Elemental analyses for ligands **1a–1i** (calculated values in parentheses)

Ligands	C	H	N
1a	67.30 (68.15)	6.78 (6.86)	15.70 (15.89)
1b	68.70 (69.45)	7.40 (7.42)	14.80 (14.72)
1c	67.90 (69.45)	7.43 (7.42)	14.90 (14.72)
1d	71.30 (71.52)	8.37 (8.31)	12.90 (12.83)
1e	71.40 (72.38)	8.55 (8.67)	12.00 (12.05)
1f	70.60 (70.56)	7.92 (7.89)	13.80 (13.71)
1g	69.60 (70.56)	7.85 (7.89)	13.70 (13.71)
1h	71.50 (71.52)	8.28 (8.31)	12.83 (12.83)
1i	74.60 (74.38)	9.45 (8.58)	10.90 (10.84)

Synthesis of Bis(chelated) Ni^{II} Complexes 2a, 2b, and 2h: Bis(chelated) Ni^{II} complexes were synthesized by addition of [NiBr₂·(C₄H₁₀O₂)] (9.7·10^{−4} mol) to a stirred solution of ligand (1.94·10^{−3} mol) in CH₂Cl₂ (7 mL). Solutions were stirred for 3 h. Complexes **2a**, **2b**, and **2h** were isolated upon concentration of the solution and addition of diethyl ether or *n*-pentane. The products precipitated as brown solids, which were filtered and dried under vacuum.

Synthesis of Monochelated Ni^{II} Complexes 2d, 2e, 2i, and 3h: Monochelated Ni^{II} complexes were prepared by addition of [NiBr₂·(C₄H₁₀O₂)] (C₄H₁₀O₂ = ethylene glycol dimethyl ether) (9.7·10^{−4} mol) to a stirred solution of ligand (1.56·10^{−3} mol) in CH₂Cl₂ (7 mL). Solutions were stirred for 3 h. For **3h**, **2d**, and **2e**, insoluble impurities were filtered off. Solutions were concentrated under vacuum to 1–2 mL, and then treated with ether. Light brown powders were filtered, washed with ether or *n*-pentane, and dried in vacuo. Insoluble **2i** precipitated as a light brown powder, which was filtered, washed with ether, and dried in vacuo.

Synthesis of Bis(chelated) Co^{III} Complexes 4a–4d, 4f–4h, 5a–5d, and 5f–5h: Syntheses of bis(chelated) Co^{III} complexes were performed by addition of the ligand (2.9·10^{−3} mol) to a stirred solution of the Co^{II} salt hexahydrate (CoCl₂·6H₂O, CoBr₂·6H₂O) (1.4·10^{−3} mol) in *n*-butanol (10 mL). Solutions were stirred for 3 h. Solids were filtered off, washed with *n*-butanol, and dried in vacuo. Crystalline precipitates were obtained by recrystallization from CH₂Cl₂/pentane or CH₂Cl₂/ether (**4a** and **5a** only). Complexes **5f**, **5h**, and **5d** are brown, while all other complexes are green.

Synthesis of Bis(chelated) Organometallic Co^{III} Complex 6g: Complex **6g** was prepared by addition of CH₃I (0.5 mL) and an excess of NaBH₄, in that order, to a stirred solution of the chloride derivative **4g** (0.16 g) in methanol (10 mL) under an inert gas. The solution was stirred at room temperature for 1 h, and the red crystalline

Table 6. Crystallographic data for compounds **1h**, **2a**, **3h**, **5b**, and **5h**

	1h	2a ·0.5CH ₂ Cl ₂	3h ·H ₂ O	5b	5h
Empirical formula	C ₁₃ H ₁₈ N ₂ O	C _{20.5} H ₂₅ Br ₂ ClN ₄ NiO ₂	C ₃₉ H ₅₆ Br ₅ N ₆ Ni ₃ O ₅	C ₂₂ H ₂₇ Br ₂ CoN ₄ O ₂	C ₂₆ H ₃₅ Br ₂ CoN ₄ O ₂
Formula mass	218.29	613.43	1264.58	598.23	654.33
Crystal system	monoclinic	monoclinic	trigonal	orthorhombic	tetragonal
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>R</i> 3̄ (no. 148)	<i>P</i> na2 ₁ (no. 33)	<i>I</i> 4̄/ <i>cd</i> (no. 110)
<i>a</i> [Å]	7.379(5)	21.737(5)	13.945(4)	15.176(7)	13.623(2)
<i>b</i> [Å]	15.635(6)	15.002(4)		8.273(3)	
<i>c</i> [Å]	11.167(5)	16.382(4)	50.665(16)	18.738(7)	29.901(8)
β [°]	93.74(5)	110.46(3)			
<i>V</i> [Å ³]	1285.6(12)	5005(2)	8532.5(44)	2352.6(16)	5549.2(19)
<i>Z</i>	4	8	6	4	8
ρ _{calcd.} [g cm ⁻³]	1.128	1.628	1.477	1.689	1.566
<i>F</i> (000)	472	2456	3786	1200	2656
μ (Mo- <i>K</i> _α) [mm ⁻¹]	0.072	4.099	4.534	4.153	3.528
θ range [°]	2.24–25.02	1.69–24.41	2.33–26.98	2.68–27.95	2.52–29.95
<i>T</i> [K]	293(2)	130(2)	293(2)	293(2)	293(2)
Reflns. collected	2394	7621	17970	3992	4153
Reflns. unique/ <i>R</i> (int)	2271/0.0730	3965/0.0509	4005/0.1358	2898/0.0580	1932/0.0690
Reflns. obsd. [<i>I</i> > 2σ(<i>I</i>)]	1592	2781	1495	1408	1246
Variables	151	296	182	179	164
<i>R</i> 1 ^[a]	0.0692	0.0596	0.0646	0.0586	0.0423
<i>wR</i> 2 ^[a]	0.0849	0.1276	0.1541	0.0997	0.0712
GOF (<i>F</i> ²) ^[b]	0.901	1.066	1.160	1.083	1.044
Residuals [e/Å ³]	0.168, −0.181	0.675, −0.770	0.981, −0.734	0.688, −0.777	0.470, −0.354

^[a] $R1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$ for observed reflections. ^[b] $GOF = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(n - p)\}^{1/2}$.

solid was then filtered off and dried in vacuo. C₂₅H₃₄CoIN₄O₂ (608.40): calcd. C 49.35, H 5.63, N 9.21; found C, 50.00, H 5.73, N 9.26. ¹H NMR (CDCl₃) δ = 1.68 (s, 3 H), 1.73 (s, 6 H), 2.12 (s, 6 H), 2.15 (s, 6 H), 2.30 (s, 6 H), 5.96 (s, 2 H), 6.60 (s, 2 H), 6.89 (s, 2 H) ppm.

X-ray Crystallographic Study: Crystal data, data collections, and refinement parameters for the structures reported are summarized in Table 6. Data sets of **1h**, **2a**, **3h**, **5b**, and **5h** were collected at room temperature by the ω/2θ scan technique with a CAD4 Enraf–Nonius diffractometer, equipped with graphite monochromator using Mo-*K*_α radiation (λ = 0.71073 Å). Intensities of three standard reflections, monitored during data collections, showed no noticeable variation in intensity for any of the crystals. Intensities were corrected for Lorentz polarization effects and data sets of **3h**, **5b**, and **5h** also for absorption, based on an empirical ψ-scan method. Diffraction data of **2a** were obtained with a Nonius DIP-1030H system with Mo-*K*_α radiation (graphite-monochromated). A total of 30 frames were collected, each with an exposure time of 20 min, over a half of reciprocal space with a rotation of 6° about the detector being located at 100 mm from the crystal. Cell refinement and data reduction were carried out with the aid of the programs Mosflm^[27] and Scala.^[27] The structures were solved by Patterson or direct methods and successive Fourier analyses (SHELXS-97)^[28] and refined by the full-matrix least-squares method based on *F*², with the aid of SHELXL-97.^[28] A difference Fourier map allowed a disordered molecule of CH₂Cl₂ to be detected (half occupancy) in **2a**, while a residual in **3h** was assigned to a water oxygen atom. All the calculations were performed with the aid of the WinGX System, version 1.64.03.^[29] CCDC-199885, -199886, -199887, -199888, and -199889 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Polymerization Reactions: The polymerization reactions were carried out by use of Schlenk techniques, under an inert gas. The AIBN and the cobalt complex were added to the dry THF solution containing MMA at 60 °C for 5 h. The amounts are reported in Table 4. The polymer was obtained as a white powder after the addition of ethanol. The powder was filtered and vacuum-dried.

Molecular Mass Measurements: The analyses were recorded with a Knauer HPLC (pump K-501, UV detector K-2501) with a PLgel 5 μm 10⁴ Å column and THF as solvent (flow rate 0.6 mL/min). Polystyrene standards were used. The polyMMA samples were dissolved as follows: 3 mg of each sample in 120 μL of 1,1,1,3,3,3-hexafluoro-2-propanol, and THF was then added up to 10 mL. The statistical calculations were performed by use of the Bruker Chromstar software program.

Acknowledgments

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- [1] D. J. Tempel, M. Brookhart, *Organometallics* **1998**, *17*, 2290–2296.
- [2] [2a] L. Johnson, M. Brookhart, C. M. Killian, S. D. Arthur, J. Feldman, E. F. McCord, S. J. McLain, K. A. Kreutzer, M. A. Bennett, E. B. Coughlin, S. D. Ittel, A. Parthasarathy, D. J. Tempel, *Wo* 96/23010, **1996**. [2b] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203.
- [3] G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. William, *Chem. Commun.* **1998**, 849–850.
- [4] T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460–462.
- [5] B. L. Small, M. Brookhart, *Macromolecules* **1999**, *32*, 2120–2130.
- [6] B. B. Wayland, G. Poszmik, S. L. Mukerjee, *J. Am. Chem. Soc.* **1994**, *116*, 7943–7944.
- [7] A. A. Gridnev, S. D. Ittel, *Chem. Rev.* **2001**, *101*, 3611–3659.

- [8] N. S. Enikopolopyan, B. R. Smirnov, G. V. Ponomarev, I. M. Belgovskii, *J. Poly. Sci. Polym. Chem. Ed.* **1981**, *19*, 879–889.
- [9] A. F. Burczyk, K. F. O'Driscoll, G. L. Rempel, *J. Polym. Sci.* **1984**, *22*, 3255–3262.
- [10] D. Kukulj, J. P. A. Heuts, T. P. Davis, *Macromolecules* **1998**, *31*, 6034–6041.
- [11] J. Halpern, F. T. T. Ng, G. L. Rempel, *J. Am. Chem. Soc.* **1979**, *101*, 7124–7126.
- [12] F. T. T. Ng, G. L. Rempel, J. Halpern, *J. Am. Chem. Soc.* **1982**, *104*, 621–623.
- [13] B. Milani, E. Stabon, E. Zangrando, G. Mestroni, *Inorg. Chim. Acta*, in press.
- [14] E. Uhlig, E. Dinjus, M. Helbig, *Z. Anorg. Allg. Chem.* **1970**, *373*, 279–284.
- [15] V. Bertolasi, G. Gilli, A. C. Veronese, *Acta Crystallogr., Sect. B* **1982**, *38*, 502–511.
- [16] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, "Typical interatomic distances: organic compounds", in *International Tables for Crystallography*, vol. C (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1995**.
- [17] [17a] U. Turpeinen, A. Pajunen, *Finn. Chem. Lett.* **1976**, 6–11.
[17b] R. J. Butchers, C. J. O'Connor, E. Sinn, *Inorg. Chem.* **1981**, *20*, 537–545.
- [18] E. Bouwman, P. Evans, H. Kooijman, J. Reedijk, A. L. Spek, *J. Chem. Soc., Chem. Commun.* **1993**, 1746–1748.
- [19] (DH)₂ = bis(dimethylglyoximate); tetradentate ligand (DO)-(DOH)pn = N²,N^{2'}-propanediylbis(2-imino-3-butanone oxime).
- [20] L. Randaccio, N. Bresciani Pahor, E. Zangrando, L. G. Marzilli, *Chem. Soc., Rev.* **1989**, *18*, 225–250.
- [21] N. Bresciani Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers, P. J. Toscano, *Coord. Chem. Rev.* **1985**, *63*, 1–125.
- [22] R. J. Gulshl, T. L. Brown, *Inorg. Chem.* **1974**, *13*, 959–965.
- [23] G. Costa, G. Mestroni, *Tetrahedron Lett.* **1967**, *41*, 4005–4007.
- [24] B. E. Daikh, R. G. Finke, *J. Am. Chem. Soc.* **1991**, *113*, 4160–4172.
- [25] B. E. Daikh, R. G. Finke, *J. Am. Chem. Soc.* **1992**, *114*, 2938–2943.
- [26] B. E. Daikh, T. J. R. Weakely, R. G. Finke, *Inorg. Chem.* **1992**, *31*, 137–139.
- [27] Collaborative Computational Project, Number 4, *Acta Crystallogr., Sect. D* **1994**, *50*, 760–763.
- [28] G. M. Sheldrick, *SHELX97, Programs for Crystal Structure Analysis*, release 97-2, University of Göttingen, Germany, **1998**.
- [29] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

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