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New unsymmetrical Schiff base Ni(II) complexes as scaffolds for dendritic and amino acid superstructures†

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Received (in Toulouse, France) 17th June 2004, Accepted 6th August 2004
First published as an Advance Article on the web 16th November 2004

An efficient stepwise *template* approach has been developed that leads to a novel Ni(II) complex of an unsymmetrical 1 : 1 : 1 Schiff base derived from *o*-phenylenediamine, benzoylacetone and salicylic aldehyde [abbreviated as salophbac Ni(II)]. The 3- and 5-hydroxysubstituted salicylic aldehydes lead to complexes containing reactive OH groups that were further employed as points of attachment for the ligand superstructures. A range of new *O*-substituted derivatives of salophbac Ni(II) complexes have been synthesized bearing *N*-protected (L)-amino acid moieties as well as poly(arylether) and poly(arylester) dendrons. New products have been characterized by means of ^{1}H and ^{13}C NMR, MS and IR data. The crystal structures of the 3-Boc–(L)-phenylalanyloxy, 3-Ac–(D,L)-alanyloxy and (3′,5′-dibenzyloxy)-3-benzyloxy derivatives of salophbac Ni(II) complexes have been determined. The supramolecular C–H$\cdots\pi$, $\pi\cdots\pi$ interactions and hydrogen bonds are discussed on the basis of the crystallographic data.

Introduction

The symmetrical 2 : 1 Schiff bases derived from salicylic aldehyde and aliphatic and aromatic 1,2-diamines, often referred to as salen and salophen, have attracted a great deal of interest in recent years due to their synthetic accessibility, their rich coordination chemistry, as well as their relevance to catalysis[1,2] and materials science.[3,4] Much less attention has been focused on unsymmetrical Schiff bases derived from 1,2-diamines, salicylic aldehyde and β-diketones.[5–16] In particular, those derived from aromatic 1,2-diamines have been relatively under-investigated[17,18] and are not yet sufficiently appreciated in the synthesis of advanced materials. It is worthwhile to mention here that unsymmetrical Schiff bases of this type seem to be of practical importance in synthesis as systems allowing the independent use of reactive centres located in their substrate-based fragments. Thus, the γ-methine position of the β-ketoimine part of the molecule is known to be a fairly reactive nucleophilic centre.[19] Another centre with different type of reactivity can be introduced into an unsymmetrical molecule provided that the salicylic aldehyde based synthon is equipped with an appropriate substituent. In consequence, each of these differently reactive sites can be independently employed in further applications of the synthetic unit thus prepared, for example in the multistep synthesis of more complex receptors.

In this project, with the aim to prepare new catalysts, the reactivity of the γ-methine group will serve to anchor the catalyst onto the solid support, whereas the reactive substituent of the salicylic aldehyde based element will be used to fine-tune the properties of the potential catalysts.

In this paper a report is given of the synthesis of novel Ni(II) complexes of an asymmetrical 1 : 1 : 1 Schiff base derived from salicylic aldehyde, *o*-phenylenediamine and benzoylacetone, abbreviated as salophbac Ni(II), **2**, and its hydroxy derivatives **3** and **4** (Scheme 1). Successful coupling reactions involving OH functions of the complexes **3** and **4** and the COOH groups of *N*-protected amino acids, as well as incorporation of dendrons bearing carboxyl and mesyl functions at their focal points, are also described.

Results and discussion

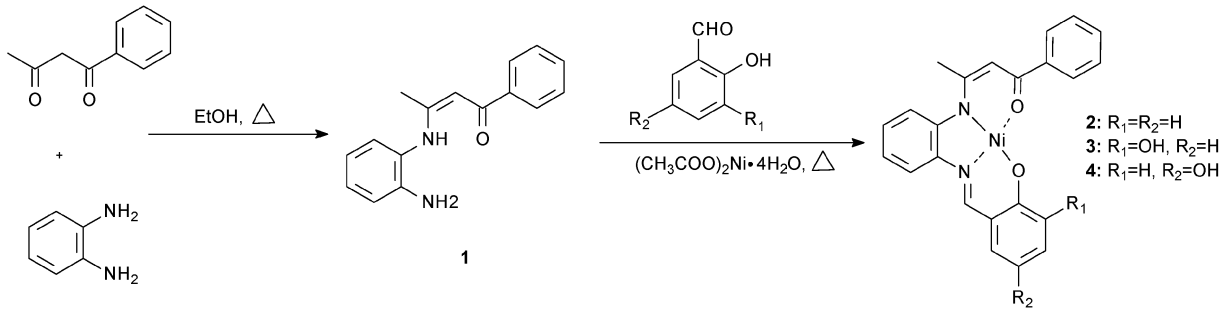
Synthesis of the complexes

Complexes 2–4. The reactions of benzoylacetone monoimine **1**[20] with salicylic aldehyde and its derivatives in the presence of nickel acetate tetrahydrate, performed according to a standard template procedure,[21] led without problems to products **2–4** in reasonable yields (Scheme 1). The products appeared analytically pure after recrystallization from ethanol (**2**) or column chromatography on silica gel, with chloroform or toluene–acetone (2 : 1) as eluents for **3** and **4**, respectively.

Evidence for the structure of products **2–4** is given by elemental analysis, ^{1}H and ^{13}C NMR data and ESI and MALDI-TOF mass spectra. Mass spectra revealed the presence of intact molecular ions ($M + H^{+}$) or ($M + Na^{+}$). The γ methine CH═ groups in **2**, **3** and **4** were easily detectable in the ^{1}H NMR spectra by the signals at δ 6.03, 5.98 and 6.22 ppm, and at δ 103,03, 103.08 and 101.90 ppm in the ^{13}C NMR, respectively. The CH═N protons resonate at δ 8.19, 8.09 and 8.61 ppm. Signals of corresponding carbons appeared at δ 165.94, 165.37 and 165.77, respectively. The C═O carbon atoms showed signals at δ 175.03, 174.43 and 172.70 ppm. The presence of OH groups in complexes **3** and **4** was manifested by ^{1}H NMR signals at δ 6.70 and 8.77 ppm, and by broad absorptions in the IR spectra at 3405 and 3110 cm^{-1}. For full

† Electronic supplementary information (ESI) available: tables of analytical and spectroscopic data; methylene proton ***a***, ***b***, ***c*** region of the ^{1}H NMR spectra of $\mathbf{3D_4}$ and $\mathbf{4D_4}$; packing diagram of complex **6**. See http://www.rsc.org/suppdata/nj/b4/b409298h/

DOI: 10.1039/b409298h



Scheme 1

analytical and spectroscopic data, see the Electronic Supplementary Information (ESI).

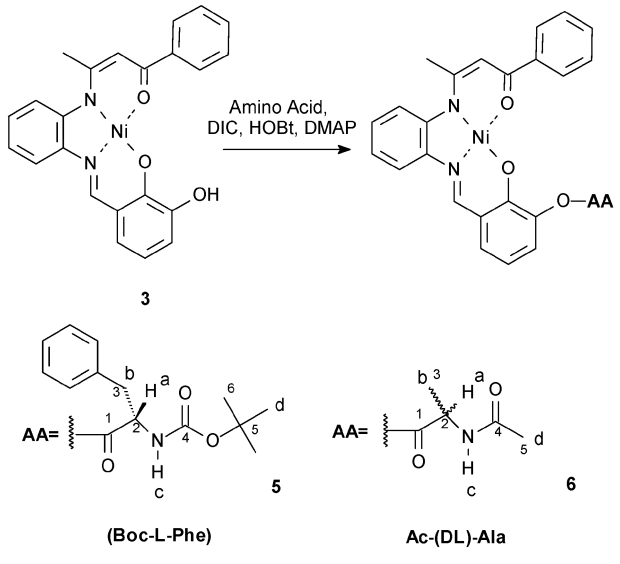
Complexes 5–11. The amino acid-salophbac conjugates **5–11** have been synthesized *via* ester linkage formation involving OH groups of complexes **3** and **4** and the corresponding COOH groups belonging to the *N*-protected L-amino acids (Boc–L-Phe, Ac–L-Ala, Boc–L-Leu, Fmoc–L-Val, Fmoc–L-Ile, Ac–L-Pro, Ac–Gly–Gly, respectively; Schemes 2 and 3). A coupling procedure widely used in peptide synthesis was employed successfully, with diisopropylcarbodiimide (DIC) as a coupling agent and a small quantity of 4-dimethylaminopyridine (DMAP) as an acylation catalyst.[22] 1-Hydroxybenzotriazole (HOBt) was also employed in order to suppress racemization.[23] The crude products were carefully purified by column chromatography [silica gel, toluene–acetone (5 : 1)], yielding pure products **5–11**.

The optical purity of the Fmoc- and Boc-*N*-protected derivatives has been proved by means of NMR experiments with Eu(tfc) as the chiral lanthanide shift reagent.[24] Unlike the Fmoc- and Boc- derivatives (**5**, **7**, **8** and **9**), Ac–Ala conjugate **6** appears to be a racemic mixture. This observation agrees well with the known mechanism of racemization involving formation and deprotonation of oxazolinones, typical for *N*-acylated amino acids.[25] The ^{1}H NMR spectra of the Ac–Pro derivative **10** revealed separate resonances corresponding to a 9 : 1 ratio of *trans* and *cis* isomers (see Table 2 in ESI).† Similar results were reported earlier for other Ac–Pro derivatives.[26–28]

Complexes $3D_1$–$3D_5$ and $4D_1$–$4D_5$. A coupling procedure similar to that described above was used in order to incorporate dendrons $\mathbf{D_1}$ and $\mathbf{D_2}$ (Fig. 1), containing COOH functions at their focal positions, synthesized by a known method.[29] New dendritically functionalized products $\mathbf{3D_1}$, $\mathbf{3D_2}$ and $\mathbf{4D_1}$, $\mathbf{4D_2}$ have been obtained in this way (Scheme 4). *O*-Alkylation has been performed using K_2CO_3 and 18C6 in order to introduce poly(arylether) dendrons ($\mathbf{D_3}$–$\mathbf{D_5}$) bearing mesyl groups at their focal points.[30–32] The products $\mathbf{3D_5}$, $\mathbf{4D_4}$ and $\mathbf{4D_5}$ appear to be amorphous, resin-like materials.

Steric interactions seem to be responsible for the remarkably lower yields of the 3-OH alkylations when using the sterically congested dendrons $\mathbf{D_4}$ and $\mathbf{D_5}$ (38 and 46%, respectively, as compared with that involving 5-OH groups (86 and 81%, respectively).

Furthermore, the ^{1}H NMR signals of internal methylene protons (*a*, see Fig. 1) belonging to dendrons attached at the 3-position of $\mathbf{3D_3}$ and $\mathbf{3D_4}$ are shifted downfield, as compared to the 5-substituted analogues ($\mathbf{4D_3}$, $\mathbf{4D_4}$). Methylene protons *a, b, c* of $\mathbf{3D_4}$ resonate at δ 5.20, 4.96 and 4.98 ppm, whereas those of $\mathbf{4D_4}$ appear at δ 4.90, 4.95 and 5.0 ppm, respectively (see ESI, methylene proton a, b, c region of ^{1}H NMR spectra).† In view of the crystallographic data obtained for crystals of complex $\mathbf{3D_3}$ (see details in the next section), the deshielding of the *a* protons seems likely to be due to C–H$\cdots\pi$ and $\pi\cdots\pi$ interactions, present also in solution.



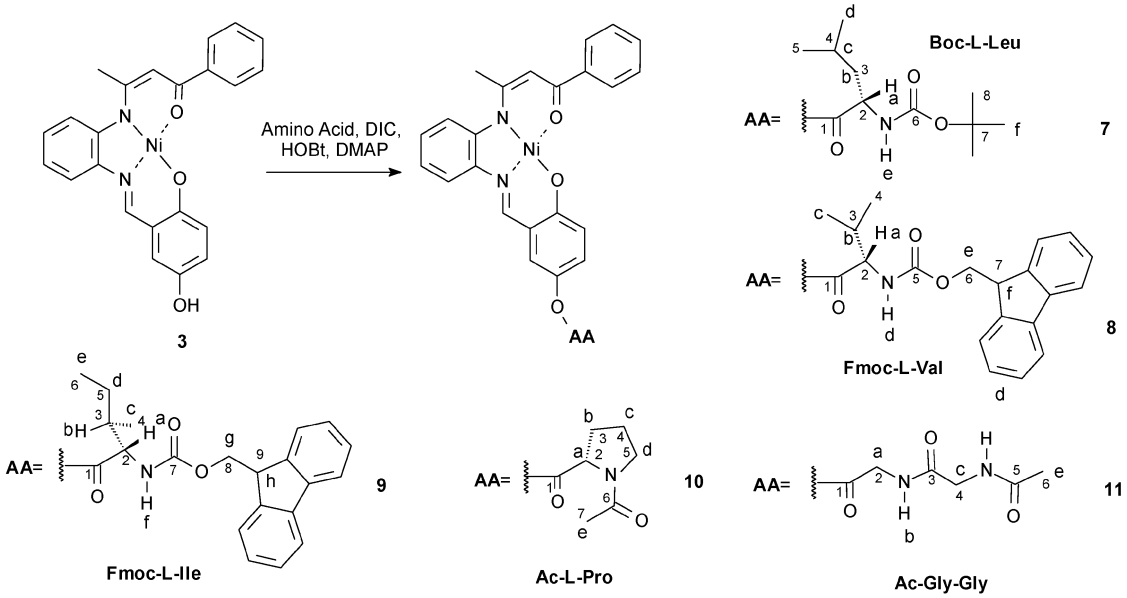
Scheme 2

Crystallography

Figs. 2, 3 and 4 show ORTEP plots of the nickel(II) complexes $\mathbf{3D_3}$, **6** and **5** with the atomic numbering scheme. Selected bonding parameters are given in Table 1. In all cases the Ni(II) atom is coordinated in a distorted square-planar configuration with two *cis*-Ni–O and *cis*-Ni–N bonds. The Ni–O bond lengths range from 1.840(1) to 1.852(3) Å, and the Ni–N ones from 1.823(3) to 1.871(2) Å, which is in agreement with those reported earlier for [bis(benzoylacetone)-*o*-phenylenediaminato(2−)]nickel(II).[33]

In complex $\mathbf{3D_3}$ the square-planar NiN_2O_2 coordination is slightly tetrahedrally distorted, with deviation of ligand atoms from the best N_2O_2 plane of up to 0.045(1) Å. In **6** this deviation is up to 0.0305(8) Å, and up to 0.080(2) and 0.095(2) Å for the two independent complexes in the asymmetric unit of **5**. In $\mathbf{3D_3}$ and **5** the Ni(II) atom lies exactly in the best N_2O_2 coordination plane within experimental error; in **6** the Ni(II) atom is 0.0247(8) Å away from this plane.

Complex $3D_3$. The supramolecular structure of compound $\mathbf{3D_3}$ is defined by extensive C–H$\cdots\pi$ interactions and intermolecular stacking between the adjacent molecules with the stacking layers approximately parallel to the (100) crystallographic plane (Fig. 5 and Table 2). Least-squares planes through adjacent units in the stacks are coplanar with a separation of *ca* 3.8 Å, and Ni$\cdots$Ni′ distances of 3.5891(7) and 3.8451(7) Å (symmetry codes of Ni′: $x, -y, 1-z$ and $1-x, -y, 1-z$, respectively). It has been recognized that in the absence of strong hydrogen-bond donors, there are extensive



Scheme 3

C–H···π and π···π interactions, which play an important role in the supramolecular assembly of aromatic compounds.[34–36]

In adjacent molecules of **3D$_3$**, the phenyl group C(51–56) is twisted by an angle of 47.6(1)° with respect to the C(41–46) ring mean plane, adopting a geometry indicative of an edge-to-face C–H···π interaction [H24···centroid C(51–56)^{i} = 2.91 Å, C24–H24···centroid C(51–56)^{i} = 129°], whilst the C(31–36) and C(41–46) rings are almost coplanar with the dihedral angle between them being 3.20(8)°. A number of π···π interactions between benzene rings is also observed.

Complex 6. Complex **6** crystallizes as a racemate, as follows from the centrosymmetric space group *C*2/*c* and the presence of both enantiomers. Fig. 3 shows a molecule with *R* chirality at the C31 atom.

The carboxyl group C30(O3)–O4 is twisted relative to the mean plane of the C(7–12) benzene ring by 83.42(9)°, corresponding to an equatorial orientation. It seems likely that it is caused by an intermolecular C13–H13···O4^{i} [symmetry code: (i) 1/2 − *x*, 3/2 − *y*, −*z*] hydrogen bond with an O···H distance of 2.45 Å and C–H···O angle of 150°.

The intermolecular N3–H30···O5^{ii} [symmetry code: (ii) 1/2 − *x*, −1/2 + *y*, 1/2 − *z*] hydrogen bonds with an O5···H30 distance of 2.01(2) Å and N–H···O angle of 158(2)° link molecules into infinite homochiral chains extended along the *b* axis (for a figure, see the ESI). An elongated π···π stacking interaction involving C(7–12) benzene rings of adjacent complexes is observed also along the *b* axis with a centroid–centroid separation of 4.036(1) Å, and at a perpendicular distance of 3.420 Å. The shortest distances between the two

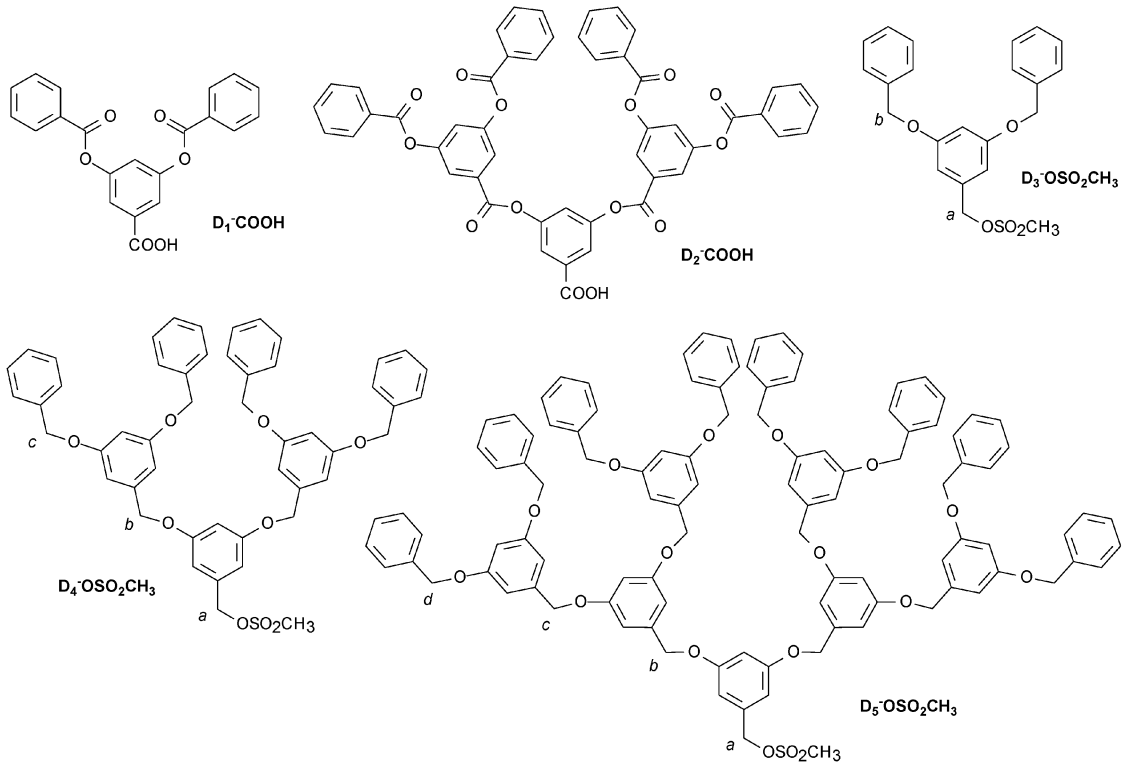
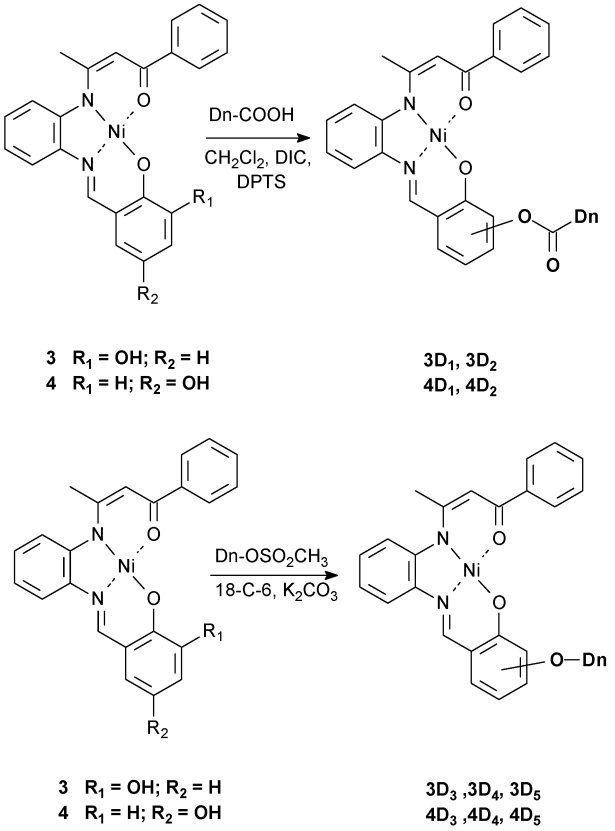


Fig. 1 Dendrons **D$_1$–D$_5$**



3 R_1 = OH; R_2 = H
4 R_1 = H; R_2 = OH

$3D_1$, $3D_2$
$4D_1$, $4D_2$

3 R_1 = OH; R_2 = H
4 R_1 = H; R_2 = OH

$3D_3$,$3D_4$, $3D_5$
$4D_3$,$4D_4$, $4D_5$

Scheme 4

Ni atoms in complex **6** are 5.2222(4) and 5.5575(4) Å, indicating a lack of metal-metal interactions.

Complex 5. The asymmetric part of the unit cell of **5** contains two different molecules and four lattice water molecules. The *S* absolute configuration at the asymmetric centre C31 (C31′ in the second molecule) was established by the Flack parameter[37] of −0.03(3). It is consistent with that assumed for Boc-(L)-phenylalanine.

The achiral parts of the two molecules are related by a pseudo-inversion centre located at (0.25, 0.266, 0.25). The chiral parts of the molecules induce the deviation from a centrosymmetric structure. The structure has a pseudo-$P2_1/c$ packing. The major difference between the molecules is the different orientations of the benzyl groups, relevant torsion angles are O4–C30–C31–C40, −10.6(6)° and −80.1(6)°, and

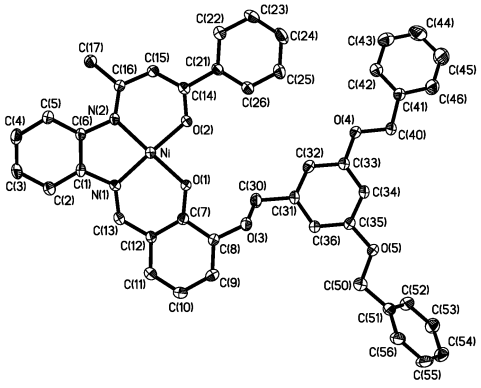


Fig. 2 The molecular structure of **$3D_3$**, showing 30% probability displacement ellipsoids with the atom numbering scheme.

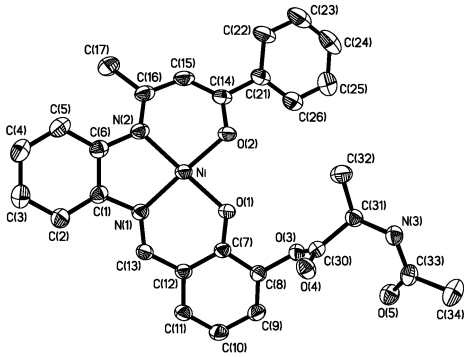


Fig. 3 The molecular structure of **6** (molecule with *R* chirality), showing 30% probability displacement ellipsoids with the atom numbering scheme.

O2–C14–C21–C26, −8.5(7)° and 27.0(6)°, for the unprimed and primed molecules, respectively.

The structure is stabilized by an extensive network of intermolecular hydrogen bonds involving lattice water molecules, N–H and C=O groups (Fig. 6). The hydrogen bonds observed in the structure are listed in Table 3.

As in the case of structure of **6**, the carboxyl group C30(O3)–O4 is twisted relative to the mean plane of the C(7–12) benzene ring by angles of 74.3(2)° and 76.4(2)° for the unprimed and primed molecules, respectively, corresponding to an equatorial orientation. It seems likely that this is caused by intermolecular C13–H13···O8′ and C13′–H13′···O8 contacts (see Table 3) that could be considered as hydrogen bonds.

The shortest distance between Ni atoms is 6.3153(9) Å, and indicates a lack of metal-metal interaction.

Conclusions

A new synthetic approach has been developed to produce a variety of structurally diverse unsymmetrical Schiff base Ni(II) complexes. Thus, a Ni(II) complex of a novel Schiff base derived from *o*-phenylenediamine, benzoylacetone and salicylic aldehyde has been synthesized and equipped with 3-OH and 5-OH substituents. It has been further shown that the reactivity of these groups can serve for the incorporation of amino acid and dendritic superstructures, recognized as being crucial for noncovalent-interaction-based phenomena.[38,39] Thus, various *N*-protected L-amino acids have been covalently attached to the Schiff base backbone, as well as poly(arylether) and poly (arylester) dendrons. The new products can serve as useful reactive building blocks, due to the nucleophilic character of the γ-methine position of the β-ketoimine moiety.

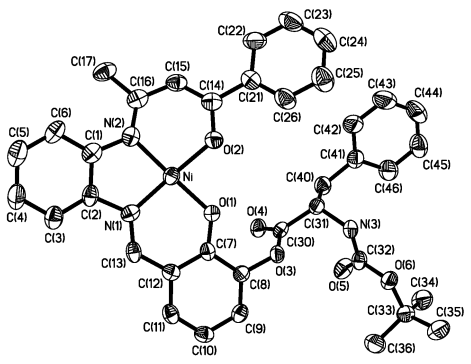


Fig. 4 The structure of the unprimed molecule in complex **5**, showing 30% probability displacement ellipsoids with the atom numbering scheme.

Table 1 Selected bond lengths (Å) and angles (°) in **3D$_3$**, **6** and **5**

	3D$_3$	**6**	**5** (unprimed molecule)	**5** (primed molecule)
Ni–O1	1.8508(17)	1.8467(13)	1.852(3)	1.842(3)
Ni–O2	1.842(2)	1.8406(13)	1.847(3)	1.836(3)
Ni–N1	1.857(2)	1.8506(16)	1.823(3)	1.849(3)
Ni–N2	1.871(2)	1.8718(15)	1.865(4)	1.868(4)
C7–O1	1.294(4)	1.297(2)	1.306(5)	1.313(4)
C14–O2	1.281(3)	1.293(2)	1.296(5)	1.299(5)
O1–Ni–O2	83.59(8)	83.38(6)	83.50(12)	83.82(12)
O1–Ni–N1	94.80(9)	94.75(6)	95.15(13)	94.96(14)
O1–Ni–N2	176.97(10)	179.38(6)	174.62(14)	174.45(15)
O2–Ni–N1	176.98(10)	176.10(7)	175.13(14)	173.65(15)
O2–Ni–N2	95.61(9)	96.10(6)	95.17(14)	95.33(14)
N1–Ni–N2	86.13(10)	85.79(7)	86.61(15)	86.48(15)

Experimental

Materials and equipment

(2-Aminophenylamino)-1-phenyl-2-buten-1-one (**1**) was prepared by a procedure described earlier.[20] Poly(arylester) and poly(arylether) dendrons (**D$_n$**–COOH, **D$_n$**–SO_2OCH_3) were synthesized according to reported procedures.[29–32] 4-Dimethylaminopyridinium *p*-toluenesulfonate (DPTS) was prepared using a known procedure.[40] Other chemicals [*N*-protected amino acids, diisopropylcarbodiimide (DIC), 4-dimethylaminopyridine (DMAP), 1-hydroxybenzotriazol (HOBt)] were purchased from commercial sources (Bachem, Aldrich, Fluka) and were used as received. Solvents were dried using standard methods and were freshly distilled before use. Silica gel 60 (Fluka) was used for column chromatography.

Elemental analyses were performed on a Euro-EA (EuroVector) microanalyzer. ^{1}H and ^{13}C NMR were run on Bruker AMX and Mercury spectrometers operating at 500 and 300 MHz, respectively. ESI and MALDI-TOF mass spectra were taken on Esquire 3000 and Bruker Reflex IV (Bruker-Daltonik, Bremen, Germany) machines, respectively. The IR spectra were recorded in KBr and hexachlorobutadiene with a Bruker IFS 48 spectrophotometer.

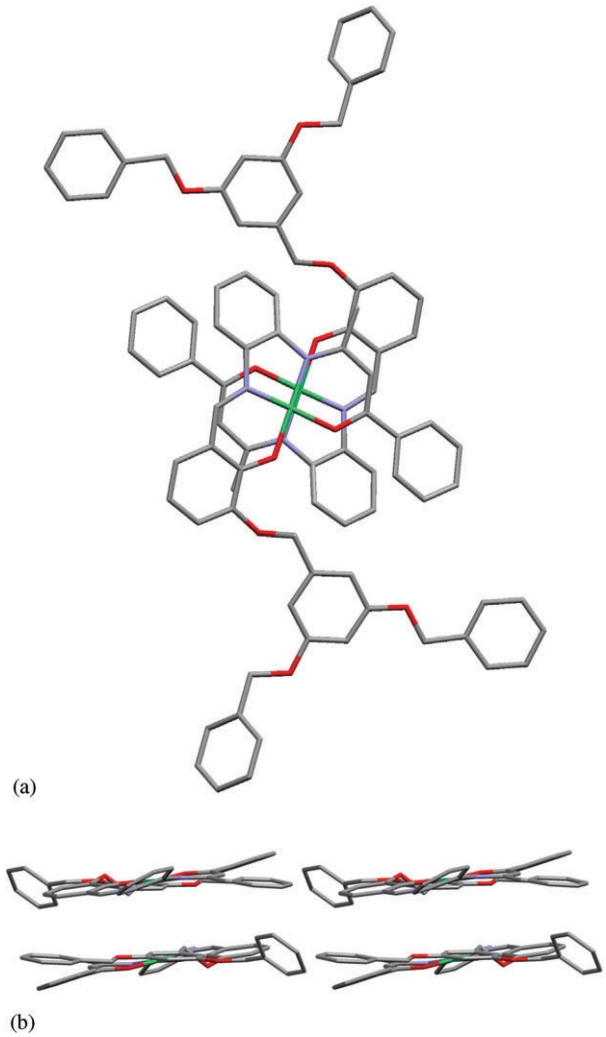


Fig. 5 (a) The stacking of two molecules of **3D$_3$** viewed along the *a* axis. Hydrogen atoms have been omitted for clarity. (b) The stacking of two molecules of **3D$_3$** viewed along the *c* axis. Hydrogen atoms have been omitted for clarity.

Table 2 Geometric parameters of the C–H···π interactions[a] in **3D$_3$**

C–H···centroid (Cg)	H···Cg/Å	C···Cg/Å	∠C–H···Cg/°
C(24)–H(24)···C(51–56)^{i}	2.91	3.563(4)	129
C(53)–H(53)···C(21–26)^{ii}	3.03	3.843(4)	147
C(55)–H(55)···C(7–12)^{iii}	3.21	4.047(4)	151
C(30)–H(302)···C(1–6)^{iv}	3.26	3.883(3)	124
C(40)–H(402)···C(31–36)^{i}	2.81	3.735(3)	159
C(50)–H(502)···C(41–46)^{i}	2.95	3.855(3)	155

[a] Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$; (iii) $-x, 1-y, -z$; (iv) $1-x, -y, 1-z$.

Syntheses

Complexes 2–4. A solution of nickel acetate tetrahydrate (1.97 g, 8 mmol) in ethanol (60 ml) was added to the warm solution prepared by dissolving **1** (4 mmol) and salicylic aldehyde (4 mmol) in ethanol (40 ml). The reaction mixture was heated under reflux for 3 h, and then left overnight at room temperature. The deep brown precipitate of complex **2** was filtered off, washed with water and then ethanol, dried and recrystallized from ethanol.

Complexes **3** and **4** were prepared by a similar procedure, starting from 2,3- and 2,5-dihydroxybenzaldehyde, respectively, and using *n*-butanol as solvent (40 and 20 ml). They were purified chromatographically [silica gel, chloroform (**3**), 2 : 1 toluene–acetone (**4**)].

Complexes 5–11 (general procedure). A solution of appropriate Fmoc- or Ac-protected amino acid (peptide; 1.5 mmol),

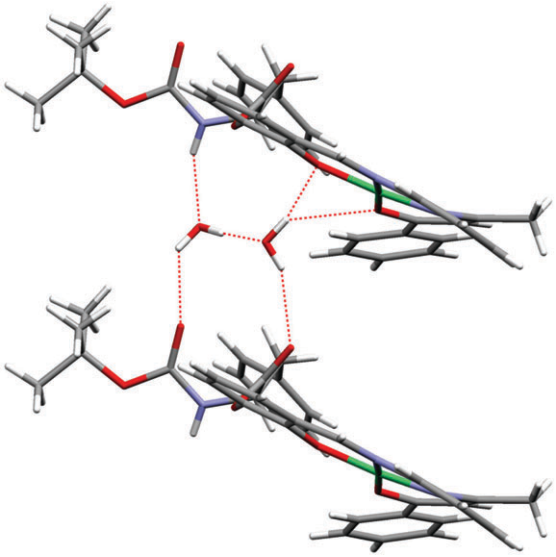


Fig. 6 Hydrogen bonds (dashed lines) connecting neighbouring unprimed molecules of **5** through two water molecules. The view is along the *c* axis.

Table 3 Hydrogen-bonding geometry[a] in **5**

D–H···A	H···A/Å	D···A/Å	∠ D–H···A/°
N3–H30···O7	2.08	2.787(6)	139
O7–H71···O8	1.93	2.742(8)	172
O7–H72···O5^{i}	2.13	2.765(6)	134
O8–H81···O4^{i}	2.19	2.935(5)	152
O8–H82···O1	2.12	2.880(5)	155
C13–H13···O8′	2.49	3.344(5)	153
N3′–H30′···O7′	2.09	2.901(7)	157
O7′–H71′···O8′	1.89	2.684(8)	162
O7′–H72′···O5′^{ii}	2.08	2.831(7)	152
O8′–H81′···O4′^{ii}	2.07	2.853(6)	160
O8′–H82′···O1′	2.23	2.841(5)	131
C13′–H13′···O8	2.56	3.418(5)	154

[a] Symmetry codes: (i) x, $y + 1$, z; (ii) x, $y - 1$, z.

HOBt (1.6 mmol) and DIC (1.6 mmol) in anhydrous dimethylformamide (20 ml) was prepared and left to stand for preactivation (5 min). This solution was then added to a solution of complex **3** or **4** (0.5 mmol) in DMF (20 ml), followed by addition of DMAP (0.2 mmol). The reaction mixture was protected from moisture and stirred at room temperature for 24 h. The crude product was precipitated from the reaction mixture by the addition of water, then filtered off and dried. It was chromatographed on a column of silica gel using toluene–acetone (5 : 1) as eluent. The main brown fraction was separated, reduced in volume to a small quantity, then diluted with *n*-hexane and allowed to crystallize. Crystals of **5** and **6** suitable for X-ray analysis were obtained by recrystallization from chloroform–n-hexane (3:1).

Complexes $3D_1$–$3D_2$ and $4D_1$–$4D_2$ (general procedure). DIC (2 mmol) was added to a solution of complex **3** or **4** (1 mmol), DPTS (0.5 mmol) and the appropriate poly(arylester) dendron (**D_1**–COOH or **D_2**–COOH) in anhydrous dichloromethane (40 ml). The reaction mixture was protected from moisture and stirred under argon for 12 h. The solvent was evaporated to dryness and the solid residue was chromatographed on a column of silica gel using diethyl ether–dichloromethane (1 : 10) as eluent. The main brown fraction was collected, concentrated to a small quantity, and then diluted with *n*-hexane to afford the pure product.

Complexes $3D_3$–$3D_5$ and $4D_3$–$4D_5$ (general procedure). A solution of complex **3** or **4** (1 mmol), the mesylate of the appropriate poly(arylether) dendron (**D_n**–OSO_2Me; 2 mmol), [18]-crown-6 (1 mmol) and K_2CO_3 (2 mmol) in anhydrous acetone (20 ml) was vigorously stirred and refluxed under argon for 12 h. After the solvent was evaporated under reduced pressure, the residue was treated with a small quantity of water (10 ml) and extracted three times with dichloromethane (30 ml). Organic layers were collected, dried with anhydrous $MgSO_4$ and evaporated to dryness. The crude product was chromatographed on a column with silica gel using diethyl ether–dichloromethane (1 : 10; compounds **$3D_3$–$3D_5$**) or *n*-hexane–diethyl acetate (1 : 10; compounds **$4D_3$–$4D_5$**). Analytical samples of **$3D_4$**, **$3D_5$** and **$4D_3$** were additionally chromatographed on preparative plates of silica gel, using dichloromethane as eluent. Crystals of **$3D_3$** suitable for the X-ray measurements were grown from ethyl acetate.

Crystallography

Intensity data for the crystal of **$3D_3$** were collected on a KUMA KM4CCD κ-axis diffractometer equipped with monochromated Mo-K_α radiation (λ = 0.71073 Å) at room temperature. The data integration and numerical absorption corrections were carried out with the CrysAlis[41] and X-RED[4] programs, respectively. Intensity data for the crystals of **6** and **5** were collected using a Bruker AXS Smart APEX CCD diffractometer with MonoCap capillary and monochromated Cu-K_α radiation (λ = 1.54178 Å) at room temperature. Data collection and data reduction were done with the SMART and SAINT-PLUS programs.[43] Empirical absorption corrections were carried out using the SADABS program.[44]

Table 4 Crystallographic data for the complexes **$3D_3$**, **6** and **5**

	$3D_3$	**6**	**5**
Formula	$C_{44}H_{36}N_2O_5Ni$	$C_{28}H_{25}N_3O_5Ni$	$C_{37}H_{35}N_3O_6Ni \cdot 2H_2O$
Formula weight	731.44	542.20	712.40
Colour	Orange-red	Dark purple	Brown
Size/mm^3	0.40 × 0.18 × 0.07	0.20 × 0.16 × 0.04	0.17 × 0.12 × 0.02
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1 (no. 2)	*C*2/*c* (no. 15)	*P*21 (no. 4)
a/Å	7.2878(5)	23.2759(3)	21.8152(3)
b/Å	14.4364(8)	8.4381(1)	7.5781(1)
c/Å	17.4246(10)	25.9355(3)	22.9560(4)
α/°	72.557(5)	90	90
β/°	85.278(5)	96.4760(10)	114.2092(7)
γ/°	82.046(5)	90	90
U/Å^3	1730.5(2)	5061.34(11)	3461.28(9)
Z	2	8	4
D_c/g cm^{-3}	1.404	1.423	1.367
μ/mm^{-1}	0.613	1.475	1.278
Measured reflect.	10591	10493	29857
Unique reflect.	6081	3956	10952
R_{int}	0.040	0.015	0.031
R_1 [$I > 2\sigma(I)$]	0.0334	0.0328	0.0437
wR_2[a] [$I > 2\sigma(I)$]	0.0524	0.0934	0.1121
R_1 (all data)	0.0810	0.0352	0.0606
wR_2[a] (all data)	0.0611	0.0953	0.1205

[a] $w = 1/[\sigma 2(F_o^2) + (aP)_2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. *a* and *b* are 0.012, 0; 0.0551, 2.4301; and 0.0683, 0.1116 for **$3D_3$**, **6** and **5**, respectively.

The structures were solved by direct methods by using the SHELXS-97 program.[45] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares based on F^2 using the SHELXL-97 program,[46] and the complete set of reflections. The final geometrical calculations were carried out with the PLATON program.[47] The relevant crystal data and experimental details are summarized in Table 4.

Hydrogen atoms were placed in their calculated positions (except for the hydrogen atoms of the water molecules, which were found in the Fourier difference map), assigned isotropic thermal parameters [1.2 times that of the attached atom (for **$3D_3$** and **5**), or refined freely (for **6**)], and allowed to ride on their respective parent atoms.‡

‡ CCDC reference numbers 255522–255524. See http://www.rsc.org/suppdata/nj/b4/b409298h/ for crystallographic data in .cif or other electronic format.

References

1 For a review, see: (*a*) E. N. Jacobsen, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH, New York, 1993, pp. 159–202; (*b*) E. N. Jacobsen, in *Comprehensive Organometallic Chemistry II*, eds. F. G. A. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. **12**, p. 1097; (*c*) T. Katsuki, *Coord. Chem. Rev.*, 1999, **140**, 189; (*d*) C. M. Che and J. S. Huang, *Coord. Chem. Rev.*, 2003, **242**, 97.

2 For selected examples of recent applications in catalysis, see: (*a*) E. N. Jacobsen, *Acc. Chem. Res.*, 2000, **33**, 421; (*b*) T. S. Reger and K. Janda, *J. Am. Chem. Soc.*, 2000, **122**, 6929; (*c*) A. Watanabe, T. Uchida, K. Ito and T. Katsuki, *Tetrahedron Lett.*, 2002, **43**, 4481; (*d*) M. Bandini, P. G. Cozzi and A. U. Ronchi, *Chem. Commun.*, 2002, 919; (*e*) C. Baleizão, B. Gigante, M. Garcia and A. Corme, *Tetrahedron Lett.*, 2003, **44**, 6813; (*f*) A. Watanabe, K. Matsumoto, Y. Shimada and T. Katsuki, *Tetrahedon Lett.*, 2004, **45**, 6229; (*g*) A. R. Silva, C. Freire and B. de Castro, *New J. Chem.*, 2004, **28**, 253.

3 S. di Bella, *Chem. Soc. Rev.*, 2001, **30**, 355 and references cited therein.

4 For selected examples, see: (*a*) S. di Bella, I. Fragalà, I. Ledoux and J. Zyss, *Chem.-Eur. J.*, 2001, **7**, 3738; (*b*) M. M. G. Antonisse, B. H. M. Snellink-Ruël, A. C. Ion, J. F. J. Engbersen and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1211; (*c*) P. Wang, Z. Hong, Z. Xie, S. Tong, O. Wong, C. S. Lee and N. Wong, *Chem. Commun.*, 2003, 1664; (*d*) C. M. Che, S. C. Chan, H. F. Xiang, M. C. W. Chan, Y. Liu and Y. Wang, *Chem. Commun.*, 2004, 1484; (*e*) K. H. Chang, C. C. Huang, Y. H. Liu, Y. H. Hu, P. T. Chou and Y. C. Lin, *J. Chem. Soc., Dalton Trans.*, 2004, 1731.

5 H. A. Kuska, M. F. Farona, P. Pappas and S. Poterton, *J. Coord. Chem.*, 1971, **1**, 259.

6 E. Kwiatkowski and M. Kwiatkowski, *Inorg. Chim. Acta*, 1980, **42**, 197.

7 K. Kasuga, T. Nagahara, M. Miyasato and Y. Yamamoto, *Inorg. Chim. Acta*, 1984, **93**, 141.

8 K. Kasuga, T. Nagahara, T. Masuda, S. Kiyota and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1631.

9 N. Matsumoto, M. Asakawa, H. Nogami and A. Ohoyoshi, *Inorg. Chim. Acta*, 1985, **96**, 87.

10 E. Kwiatkowski and M. Kwiatkowski, *Inorg. Chim. Acta*, 1986, **117**, 145.

11 T. Nagahara, M. Suzuki and K. Kasuga, *Inorg. Chim. Acta*, 1988, **149**, 279.

12 J. P. Costes, G. Cros, F. Muratet and M.-H. Darbieu, *Polyhedron*, 1987, **6**, 995.

13 J. P. Costes, *Inorg. Chim. Acta*, 1987, **130**, 17.

14 D. M. Boghaei and S. Mohebi, *J. Chem. Res. (S)*, 2001, 224.

15 E. Kwiatkowski, M. Klein and G. Romanowski, *Inorg. Chim. Acta*, 1999, **293**, 115.

16 M. S. Ray, R. Bhattacharya, S. Chaudhuri, L. Righi, G. Bocelli, G. Mukhopadhyay and A. Ghosh, *Polyhedron*, 2003, **22**, 617.

17 N. T. S. Phan, D. H. Brown, H. Adams, S. E. Spey and P. Styring, *J. Chem. Soc., Dalton Trans.*, 2004, **9**, 1348.

18 E. M. Opozda, W. Łasocha and B. Włodarczyk-Gajda, *Z. Anorg. Allg. Chem.*, 2004, **630**, 597.

19 (*a*) J. Eilmes, M. Ptaszek, Ł. Dobrzycki and K. Woźniak, *Polyhedron*, 2003, **22**, 3299 and references cited therein; (*b*) K. A. Goldsby, A. J. Jircitano, D. M. Minahan, D. Ramprasad and D. H. Busch, *Inorg. Chem.*, 1987, **26**, 2651.

20 M. Sulca, A. Y. Strakov and I. Hirsbergs, *Latv. PSR. Zinat. Akad. Vestis Ser. Chim.*, 1971, **2**, 186.

21 (*a*) E. H. Charles, L. M. L. Chia, J. Rothery, E. L. Watson, E. J. L. McInnes, R. D. Farley, A. J. Bridgeman, F. E. Mabbs, C. C. Rowlands and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 1999, 2087; (*b*) J. M. Bellerby, J. H. Morris and W. E. Smith, *Inorg. Chim. Acta*, 1985, **96**, 209.

22 D. A. Wellings and E. Atherton, in *Solid-Phase Peptide Synthesis, Methods in Enzymology*, **vol. 289**, ed. G. B. Fields, Academic Press, 1997, section I, ch. 4, p. 44.

23 M. Bodanszky, *Peptide Chemistry*, Springer, Berlin, 1988, ch. 8.

24 R. R. Fraser, in *Asymmetric Synthesis*, ed. J. D. Morrison, , 1983, vol. **1**, p. 173.

25 M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 1977, **99**, 6262.

26 B. P. Roques, S. Combrisson and R. Wasylishen, *Tetrahedron*, 1976, **32**, 1517.

27 R. N. Hunston, I. P. Gerothanassis and J. Lauterwein, *J. Am. Chem. Soc.*, 1985, **107**, 2654.

28 A. H. Sijpkes and G. Somsen, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 2563.

29 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1992, **114**, 8405.

30 B. Forier and W. Dehaen, *Tetrahedron*, 1999, **55**, 9829.

31 C. Hawker and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.*, 1990, 1010.

32 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.

33 J. Eilmes, M. Basato and G. Valle, *Inorg. Chim. Acta*, 1999, **290**, 14.

34 G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond, in Structural Chemistry and Biology*, Oxford University Press, New York, 1999.

35 Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawa and M. Nishio, *Tetrahedron*, 1999, **55**, 10047.

36 L. Z. Hua, D. C. Ying, L. J. Hui, L. Y. Jiang, M. Y. Hua and Y. X. Zeng, *New J. Chem.*, 2000, **24**, 1057.

37 H. D. Flack, *Acta Crystallogr., Sect. A.*, 1983, **39**, 876.

38 (*a*) G. W. Gokel, *Chem. Commun.*, 2003, 2847; (*b*) O. Yamauchi, A. Odani and M. Takani, *J. Chem. Soc., Dalton Trans.*, 2002, 3411.

39 (*a*) P. J. Gittins and L. J. Twyman, *Supramol. Chem.*, 2003, **15**, 5; (*b*) L. J. Twyman and A. S. H. King, *J. Chem. Res. (S)*, 2002, 43; (*c*) D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991.

40 V. Percec, G. Johansson, J. Heck, G. Ungard and S. V. Battyb, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1411.

41 *Xcalibur CCD System, CrysAlis Software System*, v. 1.170, Oxford Diffraction, Ltd., Abingdon, England, 2003.

42 *X-RED 1.18*, Stoe & Cie, GmbH, Darmstadt, Germany, 1999.

43 *SMART and SAINT-PLUS: Area Detector Control and Integration Software*, v. 5.629 and 6.45, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, 2003.

44 G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, v. 2.10, Institute for Inorganic Chemistry, University of Göttingen, Germany, 2003.

45 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.

46 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

47 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2004.