# Three heterotrinuclear Schiff base complexes of nickel(II) with cobalt(II), copper(II) and manganese(II)

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The title compounds, bis(dimethylformamide)-$1\kappa O,3\kappa O$-bis{$\mu$-2,2'-[2,2'-dimethylpropane-1,3-diylbis(nitrilomethylidyne)]diphenolato}-$1\kappa^4 N,N',O,O':2\kappa^2 O,O';2\kappa^2 O,O':3\kappa^4 N,N',O,O'$-di-$\mu$-nitrito-$1:2\kappa^2 N:O;2:3\kappa^2 O:N$-dinickel(II)cobalt(II), [CoNi$_2$(NO$_2$)$_2$(C$_{19}$H$_{22}$N$_2$O$_2$)$_2$(C$_3$H$_7$NO)$_2$], (I), -copper(II), [CuNi$_2$(NO$_2$)$_2$(C$_{19}$H$_{22}$N$_2$O$_2$)$_2$(C$_3$H$_7$NO)$_2$], (II), and -manganese(II), [MnNi$_2$(NO$_2$)$_2$(C$_{19}$H$_{22}$N$_2$O$_2$)$_2$(C$_3$H$_7$NO)$_2$], (III), consist of centrosymmetric linear heterotrinuclear metal complexes. The three complexes are isostructural. There are three bridges across the Ni–$M$ atom pairs ($M$ is Co$^{2+}$, Cu$^{2+}$ or Mn$^{2+}$) in each complex, involving two O atoms of a $\mu$-$N,N'$-bis(salicylidene)-2,2'dimethyl-1,3-propanediaminate ligand and an N—O moiety of a $\mu$-nitrito group. The coordination sphere around each metal atom, whether Co$^{2+}$, Cu$^{2+}$, Mn$^{2+}$ or Ni$^{2+}$, can be described as distorted octahedral. The Ni$\cdots M$ distances are 2.9988 (5) Å in (I), 2.9872 (5) Å in (II) and 3.0624 (8) Å in (III).

## Comment

The investigation of metal–metal multiple bonds in transition metal complexes is an important and interesting subject in inorganic chemistry. The synthesis and analysis of octahedrally coordinated tribridged Ni$\cdots M\cdots$Ni linear or non-linear homo- or hetero- di- and trinuclear complexes have been the focus of several studies (Fukuhara *et al.*, 1990; Gerli *et al.*, 1991).

The study of the intramolecular magnetic interactions in this type of complex helps to improve understanding of the magnetic exchange mechanism on a structural basis, using molecular orbital considerations. Therefore, the magnetic properties of such complexes are under investigation.

We have recently reported the structures of several dimers and trimers with SALPD$^{2-}$ ligands [SALPD$^{2-}$ is $N,N'$-bis-(salicylidene)-1,3-propanediaminate] (Ülkü, Ercan *et al.*, 1997;

Ülkü, Tahir *et al.*, 1997; Ercan & Atakol, 1998; Tahir *et al.*, 1998; Arıcı *et al.*, 1999; Atakol *et al.*, 1999; Ercan *et al.*, 1999). We report here the structures of three new linear heterotrinuclear Ni$^{2+}$ complexes, *i.e.* (I), (II) and (III).
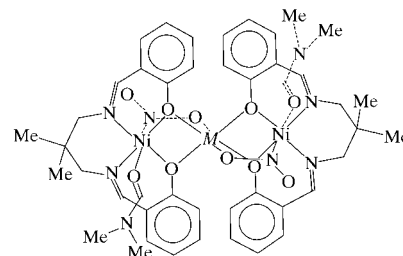


(I)   $M$ = Co
(II)  $M$ = Cu
(III) $M$ = Mn

The unit cells of the three title complexes contain two centrosymmetric trinuclear [$M${Ni(NO$_2$)(dmSALPD$^{2-}$)(dmf)}$_2$] molecules ($M$ is Co$^{2+}$, Cu$^{2+}$ or Mn$^{2+}$, dm is dimethyl and dmf is dimethylformamide), with the central $M$ ions located on an inversion centre.

The Ni$\cdots M$ pairs in these complexes are linked by two O atoms of a dmSALPD$^{2-}$ ligand, and by an N and an O atom of a nitrite group. The coordination sphere around each of the Ni, Co, Cu and Mn atoms can be described as a polyhedron. The distortions of the coordination polyhedra around Ni and $M$ from octahedral to trigonal prismatic have been calculated using the $\tau$ models of Muetterties & Guggenberger (1974) and Addison *et al.* (1984). The resulting values of $\tau_{Ni}$ are 0.013 in (I), 0.017 in (II) and 0.020 in (III), indicating that the polyhedra are close to octahedral. The central $M$ ions in the three complexes have octahedral coordination environments, with a total of six O atoms in their coordination spheres, four from the dmSALPD$^{2-}$ ligands in the equatorial planes [atoms O2, O3, O2$^i$ and O3$^i$; symmetry code: (i) $-x, -y, -z$] and two from the bridging nitrite groups in the apical positions. The $M$—O bond distances range from 2.0537 (16) to 2.160 (2) Å in (I), from 2.040 (3) to 2.107 (3) Å in (II) and from 2.1274 (16) to 2.270 (3) Å in (III).

The two terminal Ni$^{2+}$ ions in the complexes, linked by the inversion centre, also have distorted octahedral coordination environments, each involving two O and two N atoms from a dmSALPD$^{2-}$ ligand, with the apical positions of the octahedron occupied by the N and O atoms from a nitrite group and a dmf ligand, respectively. The Ni—N and Ni—O bond-distance ranges are 2.007 (2)–2.113 (3) and 2.0008 (18)–2.169 (2) Å, respectively, in (I), 2.011 (3)–2.131 (4) and 2.004 (3)–2.186 (3) Å, respectively, in (II), and 2.017 (2)–2.125 (3) and 2.0167 (18)–2.169 (2) Å, respectively, in (III).

The Ni$^{2+}$ ions lie only 0.024 (2) Å in (I), 0.031 (2) Å in (II) and 0.0383 (18) Å in (III) out of the equatorial plane defined by O2/O3/N1/N2. The dihedral angles between this equatorial plane around the Ni$^{2+}$ ions and the equatorial plane defined by O2/O3/O2$^i$/O3$^i$ around the $M$ ions are 30.88 (8)° in (I), 31.40 (2)° in (II) and 31.83 (2)° in (III). The Ni—O—$M$—O four-membered bridging ring is not planar but is roof-shaped. The chelate rings formed by Ni/N1/C8–C10/N2 in all three
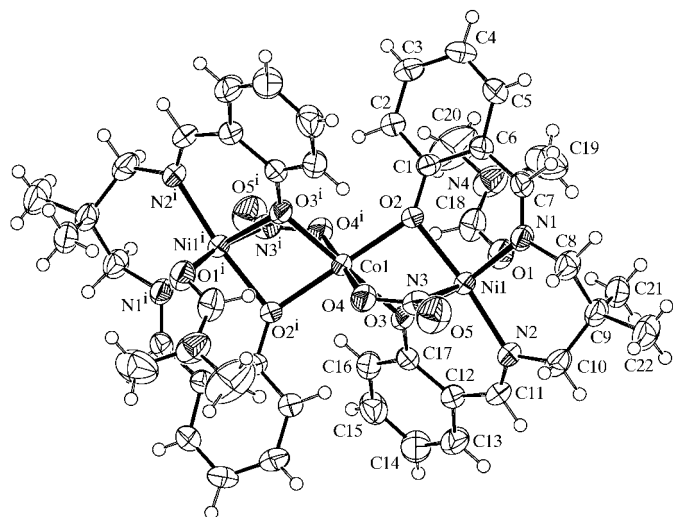
**Figure 1**
A view of the molecule of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $2 - x, -y, -z$].

compounds have a boat conformation. The distances of the two *para*-positioned boat atoms, Ni and C9, from the best plane of the other four atoms (N1/C8/C10/N2) are $-0.066$ (2) and $-0.201$ (2) Å, respectively, in (I), $-0.075$ (2) and $-0.181$ (15) Å, respectively, in (II), and $-0.0768$ (18) and $-0.167$ (16) Å, respectively, in (III).

Table 4 compares the structural data for the three complexes presented here and four other similar complexes, the dihedral angles between the two equatorial planes of neighbouring polyhedra ($\varphi$), and between the Ni$-$O$-M-$O bridging plane and the coordination plane (O2/O3/O2$^i$/O3$^i$) around the central atom ($\kappa$), along with the related distance ranges and bridging angles.

The stereochemistry of the bridging groups around the metal atoms is very important for Ni$\cdots M$ distances. If the $\mu$-bridging group across Ni$\cdots M$ is an acetato group, the $\mu$-bridge consists of coordination through three atoms. In this instance, the Ni$\cdots M$ distance is usually greater than 3.0 Å, as seen in Table 4, for compounds (IV)–(VI). If the bridging group is a nitrito group, the $\mu$-bridge consists of coordination through two atoms. In this instance, the N atom of a $\mu$-nitrito group can be directly coordinated to the metal atom and the Ni$\cdots M$ distance is less than that of the $\mu$-acetato complex. This is seen in Table 4 for compounds (I), (II), (III) and (VII), which have $\mu$-nitrito groups instead of $\mu$-acetato bridges, and their Ni$\cdots M$ distances are similar.
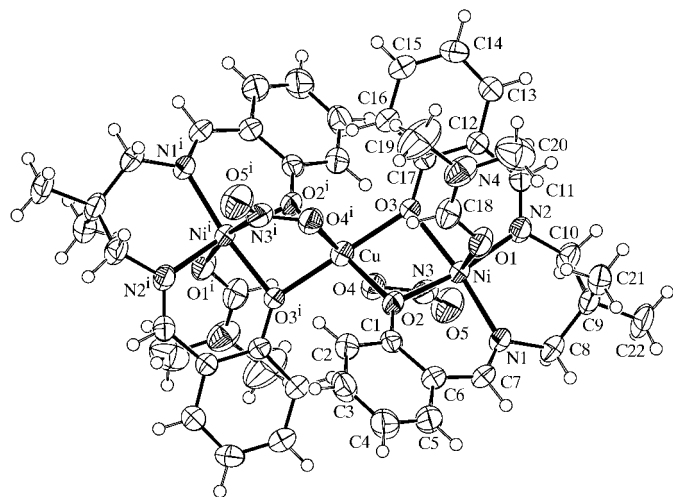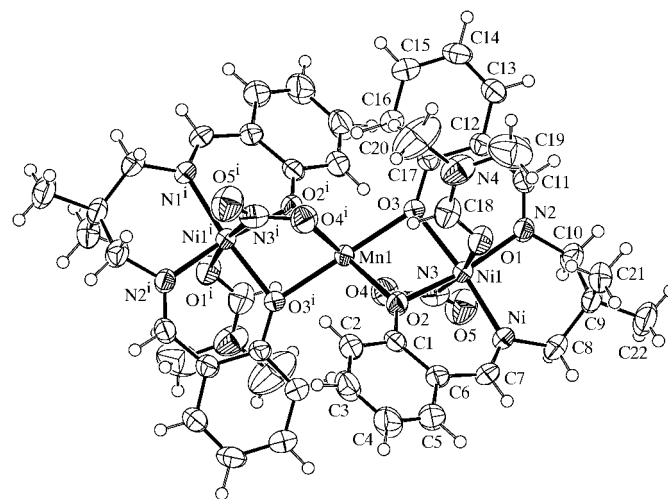


**Figure 3**
A view of the molecule of (III) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $2 - x, -y, -z$].

We conclude that the bridging angles and Ni$\cdots M$ distances seem to play a significant role in determining the strength and sign of the exchange coupling constant in distorted octahedrally coordinated Ni$\cdots M$ dimers and trimers.

## Experimental

To a solution of $N,N'$-bis(salicylidene)-2,2′-dimethyl-1,3-propanediamine (1.410 g, 5 mmol) in hot ethanol (50 ml) were added 20% ammonia solution (10 ml) and a solution of NiCl₂·6H₂O (1.185 g, 5 mmol) in hot water (30 ml). The resulting mixture was set aside for 2 h. The light-green nickel complex which formed was filtered and dried in an oven at 423 K for 3 h. This complex (0.367 g, 1 mmol) was dissolved in hot dimethylformamide (50 ml) and the temperature of the solution was increased to 383 K. A solution of CoCl₂·6H₂O (0.120 g, 0.5 mmol) for the Co complex, (I), CuCl₂·2H₂O (0.085 g, 0.5 mmol) for the Cu complex, (II), or MnCl₂·4H₂O (0.99 g, 0.5 mmol) for the Mn complex, (III), in hot MeOH (20 ml), and a solution of NaNO₂ (0.069 g, 1 mmol) in hot water (5 ml), were added slowly to this solution. The resulting mixture was set aside for 1 d. The crystals which formed were filtered off and dried in air.



**Figure 2**
A view of the molecule of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $2 - x, -y, -z$].

## Compound (I)

### Crystal data

[CoNi$_2$(NO$_2$)$_2$(C$_{19}$H$_{22}$N$_2$O$_2$)$_2$-(C$_3$H$_7$NO)$_2$]
$M_r = 1031.30$
Monoclinic, $P2_1/n$
$a = 10.942 (2)$ Å
$b = 10.2230 (10)$ Å
$c = 21.092 (2)$ Å
$\beta = 101.240 (10)°$
$V = 2314.1 (5)$ Å$^3$
$Z = 2$

$D_x = 1.480$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.3–26.0°$
$\mu = 1.23$ mm$^{-1}$
$T = 299 (2)$ K
Prism, dark brown
$0.25 \times 0.18 \times 0.13$ mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical via $\psi$ scans (Fair, 1990)
$T_{min} = 0.812$, $T_{max} = 0.865$
8277 measured reflections
4548 independent reflections
3019 reflections with $I > 2\sigma(I)$

$R_{int} = 0.030$
$\theta_{max} = 26°$
$h = -13 \rightarrow 9$
$k = -12 \rightarrow 0$
$l = -25 \rightarrow 25$
3 standard reflections
 frequency: 120 min
 intensity decay: 0.9%

### Refinement

Refinement on $F^2$
$R(F) = 0.031$
$wR(F^2) = 0.085$
$S = 1.02$
4548 reflections
346 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.4521P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.049$
$\Delta\rho_{max} = 0.30$ e Å$^{-3}$
$\Delta\rho_{min} = -0.27$ e Å$^{-3}$

### Table 1
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| N1—Ni | 2.006 (2) | O2—Co | 2.0601 (18) |
| N2—Ni | 2.016 (2) | O3—Ni | 2.0007 (18) |
| N3—Ni | 2.113 (3) | O3—Co | 2.0542 (16) |
| O1—Ni | 2.169 (2) | O4—Co | 2.161 (2) |
| O2—Ni | 2.0178 (16) | Ni—Co | 2.9988 (5) |
| | | | |
| Ni—O2—Co | 94.67 (7) | N2—Ni—N3 | 97.64 (9) |
| Ni—O3—Co | 95.38 (7) | O2—Ni—N3 | 82.29 (8) |
| O3—Ni—O2 | 81.02 (7) | O3—Co—O2 | 78.76 (7) |
| O3—Ni—N3 | 86.18 (9) | O3—Co—O4 | 95.34 (7) |
| N1—Ni—N3 | 95.33 (10) | O2—Co—O4 | 96.84 (7) |

## Compound (II)

### Crystal data

[CuNi$_2$(NO$_2$)$_2$(C$_{19}$H$_{22}$N$_2$O$_2$)$_2$-(C$_3$H$_7$NO)$_2$]
$M_r = 1035.91$
Monoclinic, $P2_1/n$
$a = 10.9520 (12)$ Å
$b = 10.2387 (13)$ Å
$c = 21.0884 (12)$ Å
$\beta = 101.252 (3)°$
$V = 2319.3 (4)$ Å$^3$
$Z = 2$

$D_x = 1.483$ Mg m$^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4.3–74.2°$
$\mu = 2.02$ mm$^{-1}$
$T = 293 (2)$ K
Prism, blue–green
$0.25 \times 0.20 \times 0.15$ mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical via $\psi$ scans (Fair, 1990)
$T_{min} = 0.632$, $T_{max} = 0.752$
4867 measured reflections
4626 independent reflections
3644 reflections with $I > 2\sigma(I)$

$R_{int} = 0.046$
$\theta_{max} = 74.2°$
$h = -13 \rightarrow 0$
$k = -12 \rightarrow 0$
$l = -25 \rightarrow 26$
3 standard reflections
 frequency: 120 min
 intensity decay: 1.1%

### Refinement

Refinement on $F^2$
$R(F) = 0.050$
$wR(F^2) = 0.159$
$S = 1.04$
4626 reflections
296 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0962P)^2 + 1.4390P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å$^{-3}$
$\Delta\rho_{min} = -1.06$ e Å$^{-3}$

### Table 2
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| Cu—O2 | 2.038 (2) | N2—Ni | 2.010 (3) |
| Cu—O3 | 2.040 (2) | N3—Ni | 2.127 (3) |
| Cu—O4 | 2.103 (2) | Ni—O2 | 2.002 (2) |
| Cu—Ni | 2.9872 (5) | Ni—O3 | 2.016 (2) |
| N1—Ni | 2.012 (3) | Ni—O1 | 2.190 (3) |
| | | | |
| O2—Cu—O3 | 79.00 (9) | N2—Ni—N3 | 95.79 (12) |
| O2—Cu—O4 | 85.98 (9) | N1—Ni—N3 | 98.35 (11) |
| O3—Cu—O4 | 84.17 (9) | O3—Ni—N3 | 81.38 (10) |
| O2—Ni—O3 | 80.43 (9) | Ni—O2—Cu | 95.34 (9) |
| O2—Ni—N3 | 85.34 (11) | Ni—O3—Cu | 94.86 (9) |

## Compound (III)

### Crystal data

[MnNi$_2$(NO$_2$)$_2$(C$_{19}$H$_{22}$N$_2$O$_2$)$_2$-(C$_3$H$_7$NO)$_2$]
$M_r = 1027.42$
Monoclinic, $P2_1/n$
$a = 11.009 (2)$ Å
$b = 10.2060 (8)$ Å
$c = 21.216 (2)$ Å
$\beta = 101.247 (7)°$
$V = 2338.0 (5)$ Å$^3$
$Z = 2$

$D_x = 1.459$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.3–26.0°$
$\mu = 1.13$ mm$^{-1}$
$T = 298 (2)$ K
Prism, light brown
$0.33 \times 0.33 \times 0.13$ mm

### Table 3
Selected geometric parameters (Å, °) for (III).

| | | | |
|---|---|---|---|
| Ni—Mn | 3.0624 (8) | O2—Ni | 2.0167 (18) |
| N1—Ni | 2.017 (2) | O2—Mn | 2.1274 (16) |
| N2—Ni | 2.023 (2) | O3—Ni | 2.0296 (16) |
| N3—Ni | 2.125 (3) | O3—Mn | 2.1283 (17) |
| O1—Ni | 2.169 (2) | Mn—O4 | 2.270 (3) |
| | | | |
| Ni—O2—Mn | 95.25 (7) | N2—Ni—N3 | 94.26 (9) |
| Ni—O3—Mn | 94.84 (7) | O3—Ni—N3 | 83.36 (8) |
| O2—Ni—O3 | 82.00 (7) | O2—Mn—O3 | 77.19 (7) |
| O2—Ni—N3 | 87.79 (9) | O3—Mn—O4 | 81.93 (7) |
| N1—Ni—N3 | 96.70 (9) | O2—Mn—O4 | 83.70 (8) |

# metal-organic compounds

**Table 4**
Structural data, bridging angles and dihedral angles ($\varphi$ and $\kappa$) for seven homo- or heterotrinuclear complexes (Å, °).

| Complex | $M-O$ | $Ni-M$ | $O-M-O$ | $\varphi$ | $\kappa$ |
|---|---|---|---|---|---|
| (I) | 2.0542 (16)–2.161 (2) | 2.9988 (5) | 78.76 (7)–96.84 (7) | 30.88 (8) | 15.42 (11)–15.50 (10) |
| (II) | 2.038 (2)–2.103 (2) | 2.9872 (5) | 79.00 (9)–85.98 (9) | 31.40 (2) | 15.61 (2)–15.83 (2) |
| (III) | 2.1274 (16)–2.270 (3) | 3.0624 (8) | 77.19 (7)–83.70 (8) | 31.83 (2) | 15.15 (2)–16.72 (2) |
| (IV) | 2.024 (3)–2.098 (3) | 3.043 (2) | 79.4 (1) | 21.9 (1) | 33.1 (1)–35.06 (7) |
| (V) | 2.260 (1)–2.293 (2) | 3.227 (5) | 73.66 (5) | 23.10 (7) | 26.38 (6)–32.80 (7) |
| (VI) | 2.163 (1)–2.194 (2) | 3.133 (2) | 76.66 (6) | 23.68 (8) | 26.91 (7)–32.36 (9) |
| (VII) | 2.048 (2)–2.103 (2) | 2.9967 (4) | 78.70 (8)–85.86 (9) | | |

Notes: (IV) is [Ni$_3$\{(CH$_3$CO$_2$)(SALPD)[(CH$_3$)$_2$SO]\}$_2$] (Ülkü, Ercan *et al.*, 1997), (V) is [CdNi$_2$\{(CH$_3$CO$_2$)(SALPD)[(CH$_3$)$_2$NCHO]\}$_2$] (Ülkü, Tahir *et al.*, 1997), (VI) is [MnNi$_2$-\{(CH$_3$CO$_2$)(SALPD)[(CH$_3$)NCHO]\}$_2$] (Ercan & Atakol, 1998) and (VII) is [CuNi$_2$\{(NO$_2$)(SALPD)[(CH$_3$)NCHO]$_2$\}$_2$] (Tahir *et al.*, 1998).

## Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scans (Fair, 1990)
 $T_{min} = 0.724$, $T_{max} = 0.879$
5026 measured reflections
4589 independent reflections
3436 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 26°$
$h = -13 \rightarrow 1$
$k = -12 \rightarrow 0$
$l = -25 \rightarrow 26$
3 standard reflections
 frequency: 120 min
 intensity decay: 1.3%

## Refinement

Refinement on $F^2$
$R(F) = 0.033$
$wR(F^2) = 0.099$
$S = 1.02$
4589 reflections
359 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.7438P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.41$ e Å$^{-3}$
$\Delta\rho_{min} = -0.54$ e Å$^{-3}$

Atoms H8*A*–H10*B* and H19*A*–H20*C* in (I), all H atoms in (II), and H19*A*–H20*C* in (III) were placed geometrically, and were refined with a riding model, with $U_{eq}(H) = 1.2U_{eq}(C)$. The positional parameters of the remaining H atoms were taken from difference maps and refined. The C—H bond lengths were in the range 0.81 (3)–0.98 (3) Å in (I) and 0.86 (4)–1.02 (3) Å in (III).

For all compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993); cell refinement: *SHELXL*97 (Sheldrick, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97.

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