# Two different structures controlled by small secondary ligands: {4-chloro-2-[2-(dimethylamino)ethylimino-methyl]phenolato}thiocyanato-nickel(II) and *catena*-poly[[{4-chloro-2-[2-(dimethylamino)ethyliminomethyl]-phenolato}nickel(II)]-*μ*-azido]

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The title complexes, $[Ni(C_{11}H_{14}ClN_2O)(NCS)]$, (I), and $[Ni(C_{11}H_{14}ClN_2O)(N_3)]_n$, (II), are two different structures constructed from the same Schiff base ligand, *viz.* 4-chloro-2-[2-(dimethylamino)ethyliminomethyl]phenol, and different linear triatomic secondary ligands, *viz.* thiocyanate for (I) and azide for (II). In mononuclear (I), the $Ni^{II}$ atom is four-coordinated in a square-planar geometry by the $N,N',O$-donor set of the Schiff base and by the N atom of the terminal thiocyanate ligand, while in polynuclear (II), the $Ni^{II}$ atom is five-coordinated in a square-pyramidal geometry by the $N,N',O$-donor set of the Schiff base and by two N atoms from two bridging azide groups.

## Comment

Transition metal complexes containing bridging ligands are currently attracting attention because of their interesting molecular topologies and crystal-packing motifs, as well as the fact that they may be designed with specific functionalities (Mukherjee *et al.*, 2001; Meyer & Pritzkow, 2001; Goher *et al.*, 2002). The prime strategy for designing these polynuclear materials is to use suitable bridging ligands (Koner *et al.*, 2003). Owing to the coordination modes of the thiocyanate and azide anions, these ligands make good bridging groups. However, given the present state of our knowledge, it is not possible to determine which coordination mode will be adopted by the thiocyanate or azide anion and whether the sought-after alternating structure will be formed (Bhaduri *et al.*, 2003; Romero *et al.*, 2002; Tercero *et al.*, 2002; Ribas *et al.*, 1999).

In the present paper, the tridentate Schiff base ligand 4-chloro-2-[2-(dimethylamino)ethyliminomethyl]phenol was used as the first ligand and was selected because it can adopt an almost fixed coordination mode through the three N- and O-donor atoms (You & Zhu, 2005; You, 2005). The secondary ligands, *viz.* the thiocyanate and azide ions, are well known bridging groups. They readily bridge different metal ions through the donor atoms, forming polynuclear complexes. Two complexes, *viz.* $[Ni(C_{11}H_{14}ClN_2O)(NCS)]$, (I), and $[Ni(C_{11}H_{14}ClN_2O)(N_3)]_n$, (II), are reported here The azide anion acts as a bridging ligand in (II) and ligates two different metal atoms through the same terminal N atom (Fig. 1). This contrasts with the monomeric structure of (I), in which the thiocyanate ligand coordinates to a single Ni atom (Fig. 2).
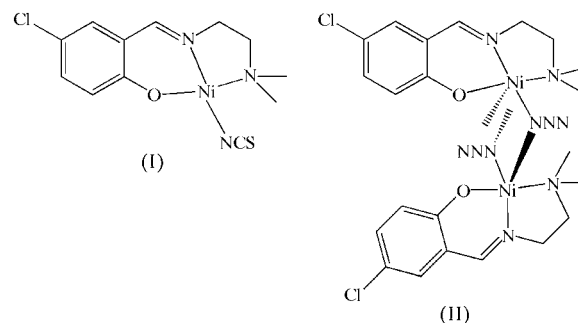


In (I), the Ni atom is four-coordinated in a square-planar geometry by the $N,N',O$-donor set of the Schiff base and by the N atom of the thiocyanate ligand. In (II), each repeat unit contains one $[Ni(C_{11}H_{14}ClN_2O)]^+$ cationic unit and one bridging azide anion. The Ni atom in (II) is five-coordinated in a square-pyramidal geometry by the $N,N',O$-donor set of the Schiff base and by two N atoms from two bridging azide groups.

In (II), all the bond lengths subtended at atom Ni1 are longer than those observed in (I) (Table 1). The coordination of the bridging N atom at the apical position of the square pyramid in (II) leads to a deviation of the metal atom from the plane of the basal donor atoms by 0.070 (2) Å, while in (I), the Ni atom lies nearly in the square plane, with a deviation of 0.009 (2) Å. In each of the complexes, the bond lengths subtended at the metal atoms are within normal ranges and, as expected, the bonds involving the pyridine N atoms are longer than those involving the imine N atoms.

The terminal thiocyanate group always adopts a nearly linear coordination mode to metal ions through the terminal N atom (Moore & Squattrito, 1999; Mondal *et al.*, 2001), while the bridging azide group easily adopts a bent coordination mode to metal ions through one of the terminal N atoms (Zhang *et al.*, 2000). In this paper, the terminal thiocyanate ligand in (I) is nearly linear and also adopts a nearly linear coordination mode with the metal atom [the N3—C12—S1 and Ni1—N3—C12 angles are 179.7 (3) and 168.1 (3)°, respectively], while the bridging azide ligand in (II) is likewise nearly linear but shows a bent coordination mode with the metal atoms [the N3—N4—N5, Ni1—N3—N4 and Ni1$^i$—N3—N4 angles are 177.6 (2), 117.80 (13) and 113.12 (13)°, respectively; symmetry code: (i) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$].

# metal-organic compounds

In conclusion, the similar small ligands used as the secondary ligands in the preparation of the title complexes severely influence the final structures.
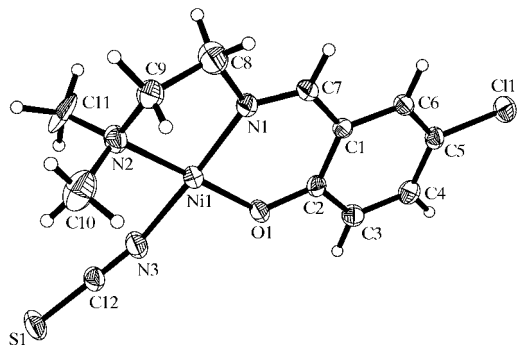


**Figure 1**
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only the major components of the disordered moiety (C8–C11/N2) are shown.
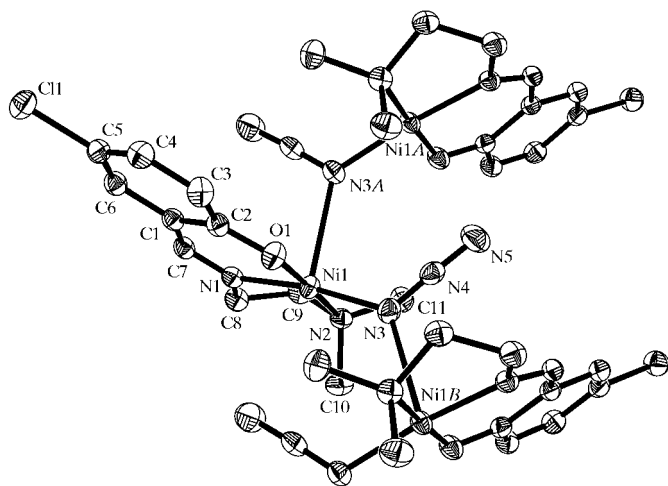


**Figure 2**
The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labeled with the suffixes $A$ and $B$ are at the symmetry positions $(x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1)$ and $(x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1)$, respectively. H atoms have been omitted.

## Experimental

For the preparation of complex (I), 5-chloro-2-hydroxybenzaldehyde (0.1 mmol, 15.6 mg) and *N,N*-dimethylethane-1,2-diamine (0.1 mmol, 8.8 mg) were dissolved in methanol (10 ml). The mixture was stirred at room temperature for about 10 min to give a clear yellow solution, to which was added an aqueous solution (2 ml) of $NH_4NCS$ (0.1 mmol, 7.6 mg) and a methanol solution (5 ml) of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.1 mmol, 24.9 mg) with stirring. The mixture was stirred for another 10 min at room temperature. After the filtrate had been kept in air for 3 d, green needle-shaped crystals had formed. Complex (II) was prepared by a procedure similar to that described for (I), with $NH_4NCS$ replaced by $NaN_3$ (0.1 mmol, 6.5 mg). Green block-shaped crystals of (II) were obtained after evaporating the solvents from the filtrate in air for a period of 8 d.

## Compound (I)

### Crystal data

| | |
|---|---|
| $[Ni(C_{11}H_{14}ClN_2O)(NCS)]$ | $D_x = 1.576$ Mg m$^{-3}$ |
| $M_r = 342.48$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 2348 |
| $a = 6.980$ (1) Å | reflections |
| $b = 10.936$ (2) Å | $\theta = 2.3$–25.4° |
| $c = 18.955$ (3) Å | $\mu = 1.67$ mm$^{-1}$ |
| $\beta = 93.901$ (2)° | $T = 298$ (2) K |
| $V = 1443.6$ (4) Å$^3$ | Needle, green |
| $Z = 4$ | $0.22 \times 0.12 \times 0.08$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART APEX area-detector diffractometer | 3293 independent reflections |
| $\omega$ scans | 2526 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan | $R_{int} = 0.043$ |
| (*SADABS*; Bruker, 2000) | $\theta_{max} = 27.5°$ |
| $T_{min} = 0.711$, $T_{max} = 0.878$ | $h = -9 \rightarrow 9$ |
| 12176 measured reflections | $k = -14 \rightarrow 14$ |
| | $l = -23 \rightarrow 24$ |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0528P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | $+ 0.4314P]$ |
| $wR(F^2) = 0.113$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.03$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3293 reflections | $\Delta\rho_{max} = 0.35$ e Å$^{-3}$ |
| 204 parameters | $\Delta\rho_{min} = -0.38$ e Å$^{-3}$ |
| H-atom parameters constrained | |

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

| | | | |
|---|---|---|---|
| Ni1—N1 | 1.840 (3) | Ni1—N3 | 1.879 (3) |
| Ni1—O1 | 1.842 (2) | Ni1—N2 | 1.953 (3) |

| | | | |
|---|---|---|---|
| N1—Ni1—O1 | 94.70 (10) | N1—Ni1—N2 | 86.38 (12) |
| N1—Ni1—N3 | 176.86 (12) | O1—Ni1—N2 | 178.89 (11) |
| O1—Ni1—N3 | 88.34 (12) | N3—Ni1—N2 | 90.58 (12) |

## Compound (II)

### Crystal data

| | |
|---|---|
| $[Ni(C_{11}H_{14}ClN_2O)(N_3)]$ | Mo $K\alpha$ radiation |
| $M_r = 326.43$ | Cell parameters from 6155 |
| Orthorhombic, *Pbca* | reflections |
| $a = 6.750$ (1) Å | $\theta = 2.5$–26.9° |
| $b = 19.893$ (2) Å | $\mu = 1.60$ mm$^{-1}$ |
| $c = 20.585$ (2) Å | $T = 298$ (2) K |
| $V = 2764.1$ (6) Å$^3$ | Block, green |
| $Z = 8$ | $0.20 \times 0.19 \times 0.10$ mm |
| $D_x = 1.569$ Mg m$^{-3}$ | |

### Data collection

| | |
|---|---|
| Bruker SMART APEX area-detector diffractometer | 3166 independent reflections |
| $\omega$ scans | 2647 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan | $R_{int} = 0.033$ |
| (*SADABS*; Bruker, 2000) | $\theta_{max} = 27.5°$ |
| $T_{min} = 0.741$, $T_{max} = 0.857$ | $h = -8 \rightarrow 8$ |
| 22079 measured reflections | $k = -25 \rightarrow 25$ |
| | $l = -26 \rightarrow 26$ |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0353P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | $+ 0.6214P]$ |
| $wR(F^2) = 0.074$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.07$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3166 reflections | $\Delta\rho_{max} = 0.38$ e Å$^{-3}$ |
| 174 parameters | $\Delta\rho_{min} = -0.21$ e Å$^{-3}$ |
| H-atom parameters constrained | |

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

| | | | |
|---|---|---|---|
| Ni1—O1 | 1.913 (2) | Ni1—N3 | 1.979 (2) |
| Ni1—N1 | 1.949 (2) | Ni1—N2 | 2.079 (2) |
| | | | |
| O1—Ni1—N1 | 93.07 (6) | O1—Ni1—N2 | 177.50 (6) |
| O1—Ni1—N3 | 89.30 (6) | N1—Ni1—N2 | 84.48 (6) |
| N1—Ni1—N3 | 172.04 (7) | N3—Ni1—N2 | 93.08 (7) |

All H atoms in the title complexes, (I) and (II), were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and with $U_{iso}$(H) values of 1.2 or 1.5 times the equivalent anisotropic displacement parameter of the parent C atom. The $C9H_2$, $C10H_3$ and $C11H_3$ groups in (I) are disordered over two distinct sites, with occupancies of 0.492 (3) and 0.508 (3). The C—C and C—N distances of the disordered groups were restrained to 1.53 (1) and 1.46 (1) Å, respectively.

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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