metal-organic compounds

Di-μ-acetato-bis{[2,4-dichloro-6-(2-pyridylmethyliminomethyl)phenolato]zinc(II)} and di-μ-thiocyanato-bis{[2,4-dichloro-6-(2-pyridylmethyliminomethyl)phenolato]copper(II)}

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The two title complexes, $[Zn_2(C_{13}H_9Cl_2N_2O)_2(C_2H_3O_2)_2]$, (I), and $[Cu_2(C_{13}H_9Cl_2N_2O)_2(NCS)_2]$, (II), are dinuclear Schiff base compounds. Both molecules are located on crystallographic centres of inversion. In (I), the Zn^{II} atom is five-coordinated in a trigonal–bipyramidal coordination, with one imine N atom of one Schiff base and two acetate O atoms defining the basal plane, and one O atom and one pyridine N atom of the Schiff base occupying the axial positions, while in (II), the Cu^{II} atom is five-coordinated in a square-pyramidal coordination, with one O and two N atoms of one Schiff base and one terminal N atom of a bridging thiocyanate ligand defining the basal plane, and one terminal S atom of another bridging thiocyanate ligand occupying the apical position. The different bridging ligands lead to the different coordinations of the complexes.

Comment

Metal–organic complexes containing bridging ligands are of current interest 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 acetate and thiocyanate anions, these ligands may act as bridging groups. A major obstacle to a more comprehensive study of such acetate- or thiocyanate-coordinated polynuclear complexes is the lack of rational synthetic procedures, since with the present state of knowledge it is hardly possible to determine which coordination mode will be adopted by the acetate anion or thiocyanate anion and whether the sought-after alternating structure will finally be formed (Bhaduri *et al.*, 2003; Romero *et al.*, 2002; Tercero *et al.*, 2002; Ribas *et al.*, 1999).

Our work is aimed at obtaining polynuclear complexes. On the basis of the above considerations, we used the rigid tridentate Schiff base ligand 2,4-dichloro-6-(2-pyridylmethyliminomethyl)phenol (DPMP) as the first ligand. The reason we use this ligand is that the rigid DPMP molecule can adopt an almost fixed coordination mode through the three N and O donor atoms (You, 2005a). The second ligand, *viz.* acetate or thiocyanate, is a well known bridging group. It readily bridges different metal ions through the donor atoms, forming polynuclear complexes. We report here two new dinuclear zinc(II) and copper(II) complexes, (I) and (II).
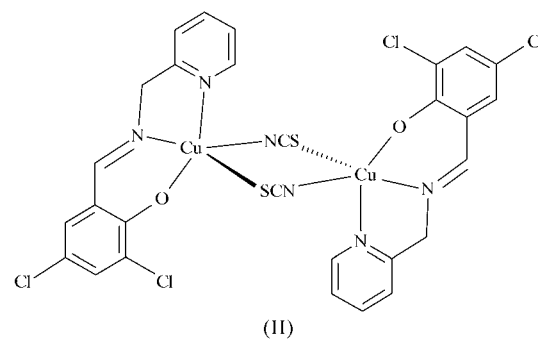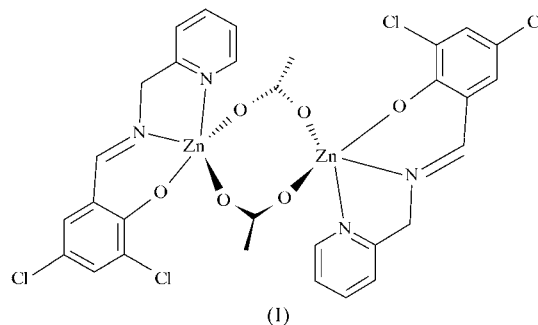
Complexes (I) and (II) are dinuclear Schiff base compounds (Figs. 1 and 2). In (I), the Zn^{II} atom is five-coordinated in a trigonal–bipyramidal coordination, with one imine N atom of one Schiff base and two acetate O atoms defining the basal plane, and one O atom and one pyridine N atom of the Schiff base occupying the axial positions. In (II), the Cu^{II} atom is five-coordinated in a square-pyramidal coordination, with one O and two N atoms of one Schiff base and one terminal N atom of a bridging thiocyanate ligand defining the basal plane, and one terminal S atom of another bridging thiocyanate ligand occupying the apical position. The different coordinations in the two complexes are caused by the different ligands bridging between the metal ions. In (I), atoms O2 and O3 of the acetate group have almost the same coordination patterns, which respectively coordinate to the Zn1 and Zn1^i atoms [symmetry code: (i) $-x + 2$, $-y$, $-z$]. The C14—O2 bond is 0.010 (4) Å longer than the C14—O3 bond (Table 1), and the Zn1—O2 bond is 0.008 (2) Å shorter than the Zn1^i—O3 bond, indicating that atom O3 adopts the ketonic coordination, while atom O2 adopts the enolic coordination. In (II), atoms N3 and S1 of the thiocyanate group have different coordination patterns. The N atom of the thiocyanate group preferentially coordinates to the metal ions through a linear

coordination mode, while the S atom of the thiocyanate group preferentially adopts an orthogonal coordination mode (You & Zhu, 2005; You, 2005b). The thiocyanate group in (II) is nearly linear and shows bent coordinations with the metal atoms [the angles N3—C14—S1, Cu1—N3—C14 and C14—S1—Cu1^{ii} are 179.1 (4), 159.3 (3) and 84.4 (3)°, respectively; symmetry code: (ii) $-x + 1, -y + 2, -z$].

Each zinc(II) moiety of complex (I) and each copper(II) moiety of complex (II) is nearly coplanar, with mean deviations from the DPMP plane of 0.043 (3) Å in (I) and 0.021 (3) Å in (II). These planar configurations can decrease the steric repulsion of the two near planar moieties. The N1—Zn1—N2 angle [77.30 (10)°] in (I) and the N1—Cu1—N2 angle [82.47 (11)°] in (II) are much smaller than 90°, a result of the strain created by the five-membered chelate rings Zn1/N2/C9/C8/N1 in (I) and Cu1/N2/C9/C8/N1 in (II). The bond 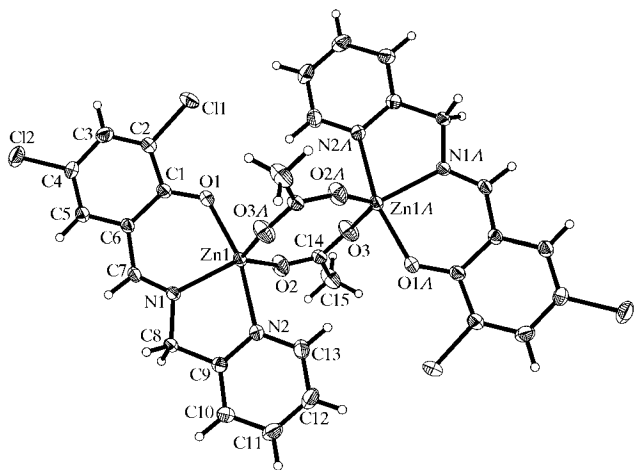lengths subtended at the metal atoms in the complexes are within normal ranges and, as expected, the bonds involving the pyridine N atoms are longer than those involving the imine N atoms.

The distance between atoms Zn1 and Zn1^{i} [4.117 (2) Å] is much shorter than that between atoms Cu1 and Cu1^{ii} [5.099 (2) Å], a result of the different sizes of the bridging ligands. The distance between atoms O2 and O3 [2.220 (4) Å] of the acetate group in (I) is much shorter than that between atoms S1 and N3 [2.784 (4) Å] of the thiocyanate group in (II). The fact that the metal–metal distance in (I) is shorter than that in (II) results in more steric repulsion of the two near planar moieties, and in the N2—Zn1—O1 angle [164.49 (10)°] in (I) deviating from 180° much more than the corresponding angle in (II) [N2—Cu1—O1 = 175.35 (11)°].

In conclusion, the different bridging ligands result in different coordinations of the complexes.

Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix A are at the symmetry position $(2 - x, -y, -z)$.
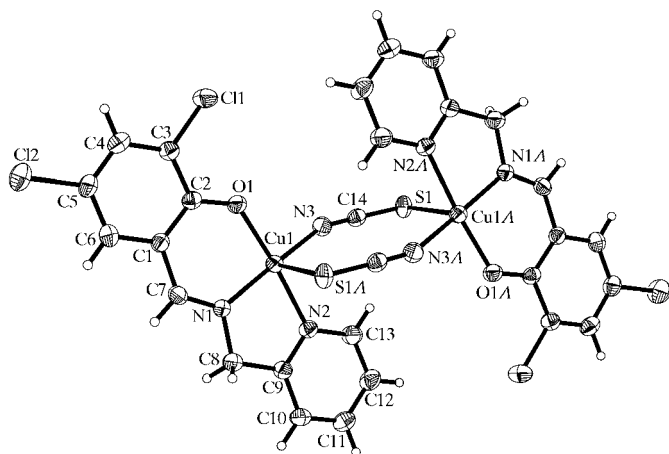

Figure 2
The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix A are at the symmetry position $(1 - x, 2 - y, -z)$.

Experimental

Compound (I)

Crystal data

[Zn$_2$(C$_{13}$H$_9$Cl$_2$N$_2$O)$_2$(C$_2$H$_3$O$_2$)$_2$]	$Z = 1$
$M_r = 809.07$	$D_x = 1.639$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.540$ (1) Å	Cell parameters from 3662
$b = 9.388$ (1) Å	reflections
$c = 12.228$ (1) Å	$\theta = 2.3$–27.6°
$\alpha = 76.208$ (1)°	$\mu = 1.84$ mm^{-1}
$\beta = 85.222$ (1)°	$T = 298$ (2) K
$\gamma = 77.320$ (1)°	Block, colourless
$V = 819.67$ (15) Å^3	0.25 × 0.22 × 0.11 mm

Data collection

Bruker SMART CCD area-detector diffractometer	3560 independent reflections
	2835 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$
	$h = -9 \rightarrow 9$
$T_{min} = 0.657$, $T_{max} = 0.823$	$k = -11 \rightarrow 11$
7858 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.463P]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
3560 reflections	$\Delta\rho_{max} = 1.02$ e Å^{-3}
209 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H-atom parameters constrained	

metal-organic compounds

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

Zn1—O2	1.989 (2)	Zn1—N2	2.164 (3)
Zn1—O3^i	1.997 (2)	O2—C14	1.244 (4)
Zn1—O1	2.013 (2)	O3—C14	1.234 (4)
Zn1—N1	2.099 (2)		
O2—Zn1—O3^i	122.65 (11)	O1—Zn1—N1	87.82 (10)
O2—Zn1—O1	99.18 (12)	O2—Zn1—N2	91.31 (11)
O3^i—Zn1—O1	92.55 (12)	O3^i—Zn1—N2	91.34 (12)
O2—Zn1—N1	115.73 (10)	O1—Zn1—N2	164.49 (10)
O3^i—Zn1—N1	120.68 (10)	N1—Zn1—N2	77.30 (10)

Symmetry code: (i) $-x + 2, -y, -z$.

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

Cu1—O1	1.913 (2)	Cu1—N2	2.034 (3)
Cu1—N1	1.922 (3)	Cu1—S1^{ii}	2.9577 (12)
Cu1—N3	1.936 (3)		
O1—Cu1—N1	93.12 (11)	O1—Cu1—N2	175.35 (11)
O1—Cu1—N3	90.77 (11)	N1—Cu1—N2	82.47 (11)
N1—Cu1—N3	169.58 (12)	N3—Cu1—N2	93.33 (12)

Symmetry code: (ii) $-x + 1, -y + 2, -z$.

Compound (II)

Crystal data

[Zn$_2$(C$_{13}$H$_9$Cl$_2$N$_2$O)$_2$(NCS)$_2$]	D_x = 1.732 Mg m^{-3}
M_r = 803.52	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1836
a = 8.718 (1) Å	reflections
b = 13.387 (2) Å	θ = 2.4–22.5°
c = 13.564 (2) Å	μ = 1.90 mm^{-1}
β = 103.305 (2)°	T = 298 (2) K
V = 1540.5 (4) Å^3	Needle, blue
Z = 2	0.15 × 0.07 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer	3505 independent reflections
	2317 reflections with $I > 2\sigma(I)$
ω scan	R_{int} = 0.059
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	θ_{max} = 27.5°
	$h = -11 \rightarrow 11$
T_{min} = 0.763, T_{max} = 0.928	$k = -17 \rightarrow 16$
13079 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.047	$w = 1/[\sigma^2(F_o^2) + (0.041P)^2]$
$wR(F^2)$ = 0.105	where $P = (F_o^2 + 2F_c^2)/3$
S = 0.99	$(\Delta/\sigma)_{max} < 0.001$
3505 reflections	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
199 parameters	$\Delta\rho_{min}$ = −0.30 e Å^{-3}

All H atoms in (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 $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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