

[*N,N'*-Bis(salicylidene)-2,2-dimethyl-1,3-propanediaminato]nickel(II) and [*N,N'*-bis(salicylidene)-2,2-dimethyl-1,3-propanediaminato]copper(II)

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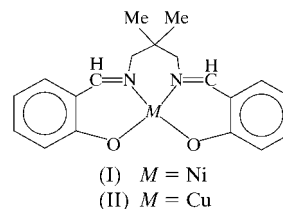
In the title compounds, {2,2'-[2,2-dimethyl-1,3-propanediyl-bis(nitrilomethylidene)]diphenolato- κ^4N,N',O,O' }nickel(II), [Ni(C₁₉H₂₀N₂O₂)], and {2,2'-[2,2-dimethyl-1,3-propanediyl-bis(nitrilomethylidene)]diphenolato- κ^4N,N',O,O' }copper(II), [Cu(C₁₉H₂₀N₂O₂)], the Ni^{II} and Cu^{II} atoms are coordinated by two iminic N and two phenolic O atoms of the *N,N'*-bis(salicylidene)-2,2-dimethyl-1,3-propanediaminate (SALPD²⁻, C₁₇H₁₆N₂O₂²⁻) ligand. The geometry of the coordination sphere is planar in the case of the Ni^{II} complex and distorted towards tetrahedral for the Cu^{II} complex. Both complexes have a *cis* configuration imposed by the chelate ligand. The dihedral angles between the N/Ni/O and N/Cu/O coordination planes are 17.20 (6) and 35.13 (7)°, respectively.

Comment

The chemistry of metal complexes with Schiff base ligands and their applications have aroused considerable attention mainly because of their preparative accessibility, diversity and structural variability. For example, there has been interest in Cu^{II}-imine-phenols because of their color isomerism (Yao *et al.*, 1997) and the Ni^{II} complexes have been used to probe the structural and electronic consequences of small modifications of the ligand skeleton (Gomes *et al.*, 1999). Nickel(II) and copper(II) complexes of diamine Schiff bases generally display square-planar coordination (Akhtar, 1981; Radha *et al.*, 1985; Drew *et al.*, 1985). We have synthesized Ni^{II}-[(SALPD)(CH₃)₂], (I), and Cu^{II}-[(SALPD)(CH₃)₂], (II), and report their structures here.

In both compounds, the structure consists of asymmetric monomers which have a monoclinic unit cell containing four molecules. In the structure of (I) (Fig. 1), the Ni atom has a square-planar coordination involving the two O and two N atoms of the tetradentate SALPD²⁻ ligand. The Ni atom is located 0.013 (3) Å from the best coordination plane

consisting of atoms N1, N2, O1 and O2, and the dihedral angle between the two Ni/N/O planes is 17.20 (6)°.



Complexes of (*N,N'*-trimethylenedisalicylideneamino)-nickel(II), [Ni(salpd)], and (*N,N'*-trimethylenedisalicylideneamino)copper(II), [Cu(salpd)] (Drew *et al.*, 1985), show similar structures to the title compounds apart from the methyl groups. Comparison of the Ni–N and Ni–O bond distances, and the O–Ni–O angles, of the present work (Table 1) with similar values in [Ni(salpd)] show them to be very similar. In the present work, the Ni–N1, Ni–N2, Ni–O1 and Ni–O2 bond distances are 1.8764 (17), 1.8660 (17), 1.8463 (14) and 1.8461 (15) Å, respectively. In [Ni(salpd)], the Ni–N and Ni–O distances are 1.901 (4) and 1.845 (3) Å,

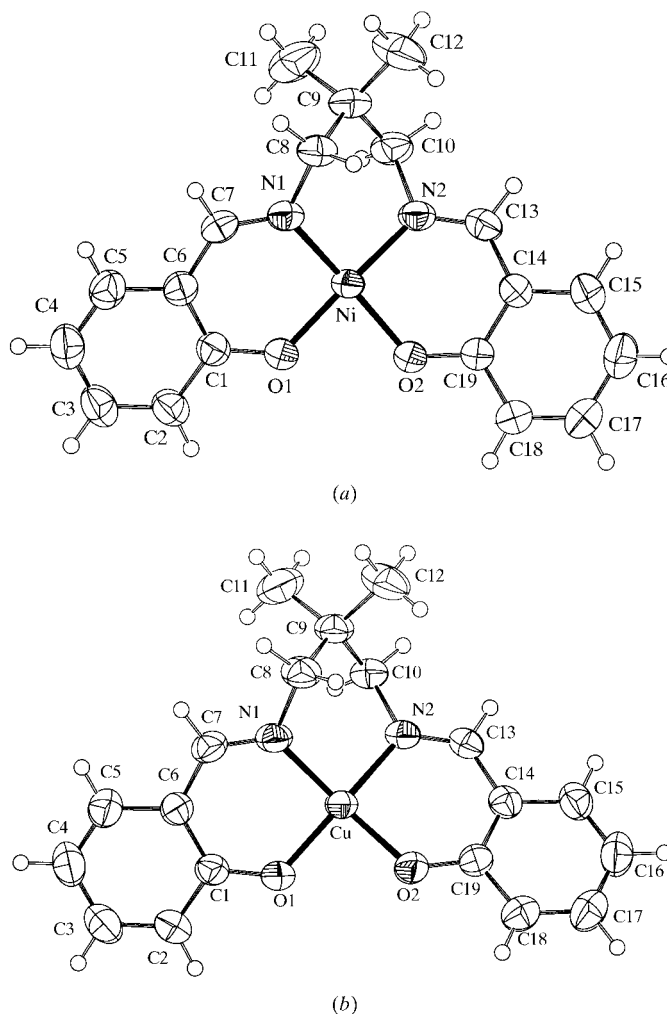


Figure 1
PLATON (Spek, 2000) drawings of (a) compound (I) and (b) compound (II). H atoms are shown as small circles of arbitrary radii and ellipsoids are shown at the 50% probability level.

respectively. The O1–Ni–O2 angle of 83.91 (7)° in (I) is greater than the value of 78.31 (13)° in [Ni(salpd)].

In the structure of (II), the Cu atom is coordinated in a distorted planar coordination geometry by two N [Cu–N1 1.929 (2) Å and Cu–N2 1.9518 (19) Å] and two O atoms [Cu–O1 1.8967 (17) Å and Cu–O2 1.8956 (17) Å] of the imine–phenol ligand (Table 2). The tetrahedral distortion between the Cu/N/O planes is 35.13 (7)°. Similar distortions are found in the literature for Cu^{II} structures. This angle between planes can be compared with the value of 21.0 (1)° for [Cu(salpd)] and 42.7 (1)° for [N,N'-bis(salicylidene)-1,4-diiminobutane]copper(II) (Yao *et al.*, 1997).

The SALPD²⁻ ligand is not planar in either compound. The chelate ring composed of atoms *M* (Ni or Cu), N1, C8, C9, C10 and N2 has a distorted boat conformation. The distances of the two *para*-positioned boat atoms, *M* and C9, from the best plane of the six atoms are 0.0001 (3) and 0.06 (2) Å for Cu, and 0.0036 (3) and 0.155 (2) Å for Ni, respectively.

Experimental

The ligand *N,N'*-bis(salicylidene)-2,2-dimethyl-1,3-propanediamine (0.620 g, 0.002 mol) was dissolved in a hot dioxane–MeOH mixture (1:1, 50 ml). To this solution were added triethylamine (1 ml) and a solution of NiCl₂·6H₂O (0.476 g, 0.002 mol) in hot MeOH (30 ml) for the preparation of the Ni complex, and a solution of CuCl₂·2H₂O (0.340 g, 0.002 mol) in hot MeOH (30 ml) for the preparation of the Cu complex. The mixtures were set aside for 2 d and the dark-brown crystals of the nickel(II) complex and dark-green crystals of the copper(II) complex which formed were filtered off and dried in an oven at 373 K.

Compound (I)

Crystal data

[Ni(C₁₉H₂₀N₂O₂)]
M_r = 367.08
 Monoclinic, *P*2₁/*n*
a = 9.9329 (12) Å
b = 15.8778 (11) Å
c = 11.8793 (10) Å
 β = 112.200 (3)°
V = 1734.6 (3) Å³
Z = 4

D_x = 1.406 Mg m⁻³
 Cu *K*α radiation
 Cell parameters from 25 reflections
 θ = 4.9–74.2°
 μ = 1.72 mm⁻¹
T = 301 (2) K
 Prism, dark brown
 0.35 × 0.30 × 0.25 mm

Data collection

CAD-4 EXPRESS diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical
 via ψ scans (Fair, 1990)
T_{min} = 0.585, *T_{max}* = 0.673
 3704 measured reflections
 3503 independent reflections
 3058 reflections with *I* > 2σ(*I*)

R_{int} = 0.036
 θ_{\max} = 74.2°
 h = -12 → 0
 k = -19 → 0
 l = -13 → 14
 3 standard reflections
 frequency: 120 min
 intensity decay: 2.2%

Refinement

Refinement on *F*²
R(*F*) = 0.036
wR(*F*²) = 0.106
S = 1.01
 3503 reflections
 218 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.6415P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$
 Extinction correction: Larson (1970)
 Extinction coefficient: 0.0072 (4)

Table 1

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

Ni–N1	1.8764 (17)	Ni–O2	1.8461 (15)
Ni–N2	1.8660 (17)	Ni–O1	1.8463 (14)
O2–Ni–O1–C1	175.94 (19)	O1–Ni–O2–C19	-162.7 (2)
N2–Ni–O1–C1	-109.6 (3)	N2–Ni–O2–C19	29.6 (2)
N1–Ni–O1–C1	9.43 (19)	N1–Ni–O2–C19	-78.4 (4)

Compound (II)

Crystal data

[Cu(C₁₉H₂₀N₂O₂)]
M_r = 371.91
 Monoclinic, *P*2₁/*n*
a = 9.7452 (12) Å
b = 17.2276 (14) Å
c = 11.3606 (10) Å
 β = 112.981 (3)°
V = 1755.9 (3) Å³
Z = 4

D_x = 1.407 Mg m⁻³
 Cu *K*α radiation
 Cell parameters from 15 reflections
 θ = 5.0–74.2°
 μ = 1.86 mm⁻¹
T = 301 (2) K
 Prism, dark green
 0.30 × 0.20 × 0.20 mm

Data collection

CAD-4 EXPRESS diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical
 via ψ scans (Fair, 1990)
T_{min} = 0.606, *T_{max}* = 0.707
 3591 measured reflections
 3419 independent reflections
 2982 reflections with *I* > 2σ(*I*)

R_{int} = 0.036
 θ_{\max} = 74.2°
 h = -11 → 12
 k = 0 → 21
 l = -14 → 0
 3 standard reflections
 frequency: 120 min
 intensity decay: 1.3%

Refinement

Refinement on *F*²
R(*F*) = 0.038
wR(*F*²) = 0.106
S = 1.04
 3419 reflections
 218 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.8826P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.47 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$

Table 2

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

Cu–O2	1.8956 (17)	Cu–N1	1.929 (2)
Cu–O1	1.8967 (17)	Cu–N2	1.9518 (19)
N2–Cu–N1–C7	147.9 (2)	O2–Cu–N2–C10	174.41 (16)
O2–Cu–N1–C8	68.8 (3)	O1–Cu–N2–C10	74.2 (2)
O1–Cu–N1–C8	170.30 (18)	N1–Cu–N2–C10	-30.13 (17)
N2–Cu–N1–C8	-34.88 (19)	O1–Cu–O2–C19	153.4 (2)
N1–Cu–N2–C13	162.3 (2)	N1–Cu–O2–C19	-104.2 (3)

H atoms bonded to C atoms were placed geometrically. All H atoms were refined as riding with *U*_{eq}(H) = 1.2*U*_{iso}(C).

For both compounds, data collection: CAD-4 EXPRESS (Enraf–Nonius, 1993); cell refinement: SHELXL97 (Sheldrick, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97; molecular graphics:

PLATON (Spek, 2000); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1331). Services for accessing these data are described at the back of the journal.

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