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### Tetraaquabis(*p*-nitrosalicylato) Complexes of Zinc(II) and Cobalt(II)

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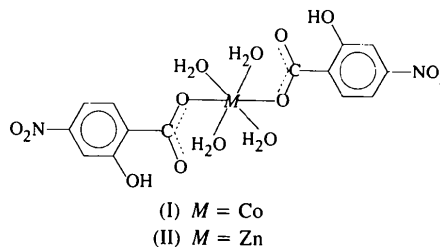
#### Abstract

In the title compounds having the general formula  $[M(C_7H_4NO_5)_2(H_2O)_4]$ , where  $M = Zn^{II}$ ,  $Co^{II}$  and  $Ni^{II}$ , the coordination polyhedron around the metal atom is a slightly distorted octahedron involving one carboxyl O atom from each *p*-nitrosalicylato ligand and the O atoms of the four water molecules. The mean  $M-O_{water}$  and  $M-O_{carboxyl}$  distances are 2.126 (1) and 2.047 (1) Å, respectively, for the zinc complex, and 2.118 (1) and 2.052 (1) Å, respectively, for the cobalt complex. Centrosymmetric monomers are cross-linked via intermolecular hydrogen bonds.

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#### Comment

The structures of metal complexes having different benzoic acid substituents have been the subject of much interest in our laboratory. The coordination properties and geometric parameters are available from the crystal structure studies of poly[bis(*p*-nitrosalicylato-*O*:*O'*)-disilver(I)-*O*<sup>3</sup>:Ag';Ag:*O*<sup>3</sup>] (Tahir, Ülkü & Movsumov, 1996a), cerium 3,5-dinitrobenzoate dihydrate (Tahir, Ülkü & Movsumov, 1996c) and monoaquabis(*p*-nitrosalicylato)lead(II) (Tahir, Ülkü & Movsumov, 1996d). Reports on zinc(II) benzoate (Guseinov, Musaev, Usabaliev, Amiraslanov & Mamedov, 1984), zinc(II) *p*-nitrobenzoate (Guseinov, Musaev, Amiraslanov, Usabaliev & Mamedov, 1983), bis(*p*-nitrobenzoato)tetraaquacobalt(II) dihydrate (Nadzhafov, Shnulin & Mamedov, 1981) and tetraaquabis(salicylato)cobalt(II) (Gupta & Mahanta, 1978) also contain structural details of a similar group of complexes. As a continuation of our investigations, we synthesized three new isomorphous metal complexes of general formula  $[M(C_7H_4NO_5)_2(H_2O)_4]$ , where  $M = Zn^{II}$ ,  $Co^{II}$  and  $Ni^{II}$ . We report here the structural parameters in detail for the cobalt(II), (I), and zinc(II), (II), complexes.



The structures consists of centrosymmetric monomers with the metal atom occupying the two inversion centers at 0,0,0 and  $0, \frac{1}{2}, \frac{1}{2}$  of the monoclinic unit cell. Slightly distorted octahedral coordination around the metal atom involves one carboxyl O atom from each *p*-nitrosalicylato ligand and the O atoms of four water molecules. The  $M-O_{water}$  distances within the basal plane of the octahedron have values between 2.086 (2)–2.151 (1) Å and 2.096 (1)–2.156 (1) Å for the Co and Zn complexes, respectively, and are longer than the  $M-O_{carboxyl}$  bonds of 2.052 (1) and 2.047 (1) Å found in the respective complexes. In the related octahedral complex tetraaquabis(3,5-dinitrobenzoato-*O*)cobalt(II) tetrahydrate (Tahir, Ülkü & Movsumov, 1996b), the  $Co-O_{water}$  distances are shorter than the  $Co-O_{carboxyl}$  distances. As can be seen from Table 3, the second carboxyl O atom of the ligand which is not coordinated to the metal atom, is involved in intermolecular hydrogen bonding with a hydroxyl group on one side and a coordinated water molecule on the other. Intermolecular hydrogen bonding between the water molecules of the coordination sphere as well as between the water molecules and the nitro O atoms constitute a three-dimensional hydrogen-bonding network in the crystal.

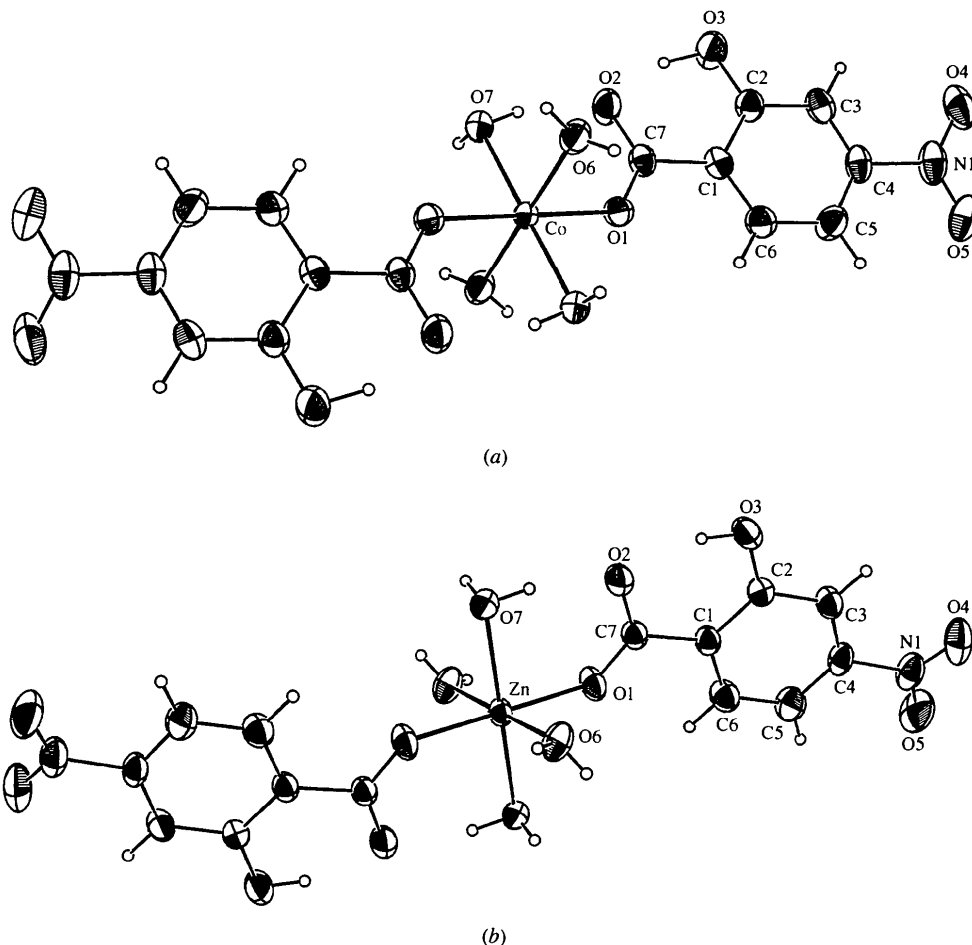


Fig. 1. ORTEPII (Johnson, 1976) drawings of (a) [Co(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] and (b) [Zn(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>], with the atomic numbering schemes. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

## Experimental

The title complexes were synthesized by the reaction of hot aqueous solutions of CoSO<sub>4</sub>·7H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O and sodium *p*-nitrosalicylate in a 1:2 stoichiometric ratio. The mixture was filtered and crystals were obtained after a few days at room temperature.

### Cobalt(II) complex

#### Crystal data

[Co(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]

*M<sub>r</sub>* = 495.222

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 5.140 (2) Å

*b* = 14.784 (3) Å

*c* = 11.941 (2) Å

β = 97.54 (5)°

*V* = 899.7 (6) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.828 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10.65–18.32°

μ = 1.03 mm<sup>-1</sup>

*T* = 295 K

Needle

0.50 × 0.20 × 0.15 mm

Orange

#### Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

empirical via ψ scans

(*MolEN*; Fair, 1990)

*T<sub>min</sub>* = 0.842, *T<sub>max</sub>* = 0.857

1649 measured reflections

1432 independent reflections

1271 reflections with

*I* > 3σ(*I*)

*R<sub>int</sub>* = 0.009

θ<sub>max</sub> = 24.0°

*h* = 0 → 5

*k* = 0 → 16

*l* = -13 → 13

3 standard reflections

frequency: 120 min

intensity decay: -0.072%

#### Refinement

Refinement on *F*

*R* = 0.027

*wR* = 0.038

*S* = 1.43

1275 reflections

142 parameters

H atoms: see below

Weighting scheme: see below

(Δ/σ)<sub>max</sub> = 0.00011

Δρ<sub>max</sub> = 0.305 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.230 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °) for the cobalt(II) complex

Co—O1	2.052 (1)	O3—C2	1.349 (3)
Co—O6	2.086 (2)	O4—N1	1.222 (3)
Co—O7	2.151 (1)	O5—N1	1.226 (3)
O1—C7	1.254 (3)	N1—C4	1.476 (3)
O2—C7	1.266 (3)	C1—C7	1.496 (3)
O1—Co—O6	88.22 (6)	C6—C1—C7	120.3 (2)
O1—Co—O7	92.57 (6)	O3—C2—C1	121.4 (2)
O6—Co—O7	88.67 (6)	O3—C2—C3	118.4 (2)
Co—O1—C7	128.3 (1)	N1—C4—C3	118.4 (2)
O4—N1—O5	123.5 (2)	N1—C4—C5	118.4 (2)
O4—N1—C4	118.2 (2)	O1—C7—O2	124.7 (2)
O5—N1—C4	118.3 (2)	O1—C7—C1	117.7 (2)
C2—C1—C7	120.8 (2)	O2—C7—C1	117.7 (2)

Table 2. Hydrogen-bonding geometry (Å, °) for the cobalt(II) complex

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3'...O2	0.982	1.603	2.525 (3)	154.60
O6—H61...O5 <sup>i</sup>	0.806	2.325	3.020 (3)	144.85
O6—H62...O7 <sup>ii</sup>	0.854	1.955	2.804 (2)	173.52
O7—H71...O3 <sup>iii</sup>	0.808	2.141	2.920 (3)	161.85
O7—H72...O2	0.846	1.833	2.656 (2)	164.12

Symmetry codes: (i)  $1 - x, -y, 1 - z$ ; (ii)  $-1 - x, -y, -z$ ; (iii)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ .

### Zinc(II) complex

#### Crystal data

[Zn(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]

$M_r = 501.659$

Monoclinic

$P2_1/c$

$a = 5.145 (3) \text{ \AA}$

$b = 14.772 (2) \text{ \AA}$

$c = 11.936 (2) \text{ \AA}$

$\beta = 97.56 (4)^\circ$

$V = 899.3 (7) \text{ \AA}^3$

$Z = 2$

$D_x = 1.852 \text{ Mg m}^{-3}$

$D_m$  not measured

#### Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

Absorption correction:

empirical via  $\psi$  scans (MolEN; Fair, 1990)

$T_{\min} = 0.749, T_{\max} = 0.801$

2033 measured reflections

1627 independent reflections

#### Refinement

Refinement on  $F^2$

$R = 0.026$

$wR = 0.033$

$S = 1.19$

1456 reflections

142 parameters

H atoms: see below

Weighting scheme: see below

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10.55\text{--}18.39^\circ$

$\mu = 1.48 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Needle

$0.5 \times 0.20 \times 0.15 \text{ mm}$

Orange

1428 reflections with

$I > 3\sigma(I)$

$R_{\text{int}} = 0.013$

$\theta_{\text{max}} = 26.32^\circ$

$h = -6 \rightarrow 0$

$k = -18 \rightarrow 0$

$l = -14 \rightarrow 14$

3 standard reflections

frequency: 120 min

intensity decay:  $-2.37\%$

$(\Delta/\sigma)_{\text{max}} = 0.00020$

$\Delta\rho_{\text{max}} = 0.355 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.200 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. Selected geometric parameters (Å, °) for the zinc(II) complex

Zn—O1	2.047 (1)	N1—C4	1.474 (3)
Zn—O6	2.096 (1)	C1—C2	1.401 (3)
Zn—O7	2.156 (1)	C1—C6	1.398 (3)
O1—C7	1.249 (3)	C1—C7	1.496 (3)
O2—C7	1.265 (3)	C2—C3	1.395 (3)
O3—C2	1.341 (3)	C3—C4	1.370 (4)
O4—N1	1.220 (3)	C4—C5	1.379 (3)
O5—N1	1.226 (3)	C5—C6	1.378 (3)
O1—Zn—O6	88.24 (6)	C6—C1—C7	119.7 (2)
O1—Zn—O7	92.19 (6)	O3—C2—C1	121.6 (2)
O6—Zn—O7	88.62 (6)	O3—C2—C3	118.3 (2)
Zn—O1—C7	128.3 (1)	N1—C4—C3	117.8 (2)
O4—N1—O5	123.7 (2)	N1—C4—C5	118.5 (2)
O4—N1—C4	118.3 (2)	O1—C7—O2	124.7 (2)
O5—N1—C4	118.0 (2)	O1—C7—C1	117.9 (2)
C2—C1—C7	120.9 (2)	O2—C7—C1	117.4 (2)

Table 4. Hydrogen-bonding geometry (Å, °) for the zinc(II) complex

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3'...O2	0.863 (2)	1.711 (2)	2.528 (3)	156.85 (14)
O6—H61...O5 <sup>i</sup>	0.775 (1)	2.341 (3)	3.016 (3)	146.27 (13)
O6—H62...O7 <sup>ii</sup>	0.754 (2)	2.060 (2)	2.813 (3)	176.55 (12)
O7—H71...O3 <sup>iii</sup>	0.754 (2)	2.195 (2)	2.916 (3)	160.49 (13)
O7—H72...O2	0.883 (1)	1.788 (2)	2.645 (2)	163.64 (12)

Symmetry codes: (i)  $1 - x, -y, 1 - z$ ; (ii)  $-1 - x, -y, -z$ ; (iii)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ .

The weighting scheme used for the two complexes was  $w = 4F^2/[\sigma(I)^2 + (pF^2)^2]$ . If  $F^2 < \text{cutoff} \times [\sigma(I)^2 + (pF^2)^2]^{1/2}$ , then reflection is omitted ( $p = 0.04$ , cutoff = 1.0 for the cobalt and 2.0 for the zinc complex). All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically 0.95 Å from their corresponding C atoms, while the H atoms of water molecules and the OH group were taken from a difference map and refined for a few cycles. For all H atoms, a riding model was used with  $B_{\text{iso}}(\text{H}) = 1.3B_{\text{eq}}(\text{C}, \text{O})$ .

For both compounds, data collection: CAD-4 Express (Enraf–Nonius, 1993); data reduction: MolEN (Fair, 1990); program(s) used to solve structures: SIMPEL in MolEN; program(s) used to refine structures: LSFM in MolEN; molecular graphics: MolEN version of ORTEPII (Johnson, 1976); software used to prepare material for publication: MolEN.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: SK1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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### Bis{2-[(2-hydroxybenzyl)iminomethyl]-phenolato(2-)-O:O,N,O'}dicopper(II)

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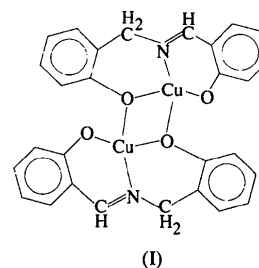
#### Abstract

The title compound,  $[\text{Cu}_2(\text{C}_{14}\text{H}_{11}\text{NO}_2)_2]$ , consists of doubly oxygen-bridged centrosymmetric copper dimers. Each Cu atom has a distorted square-planar environment involving three O atoms and an N atom of the ligands. The Cu—O distances in the coordination plane vary from 1.881 (8) to 1.930 (10) Å and the Cu—N distance is 1.920 (10) Å. In the bridging plane, the Cu—O—Cu' and O—Cu—O' angles are 103.5 (4) and 76.5 (3)°, respectively. The Cu···Cu' distance is 3.073 (2) Å.

#### Comment

It is well known that dimeric copper(II) complexes with double oxygen bridges have subnormal magnetic moments due to the super-exchange mechanism over the O atoms (Kato, Jonassen & Fanning, 1964; Butcher & Sinn, 1975; Kato & Muto, 1988). The ligand stereochemistry around the Cu atom and the structure of the double bridge influences the magnetic properties. As an extension of our structural studies of the doubly oxygen-bridged dimeric copper complexes, of which

bis[4-[(5-chloro-2-hydroxyphenyl)imino]-2-penten-2-olato-O,O',N}copper(II)] (Tahir, Ülkü, Atakol & Akay, 1996) and bis[4-[(2-oxylbenzyl)imino]-2-penten-2-olato-O,O',N}copper(II)] (Ülkü, Tahir, Atakol & Tastekin, 1997) have been published, we report here the structure of the title compound,  $[\text{Cu}_2(\text{C}_{14}\text{H}_{11}\text{NO}_2)_2]$ , (I). These structures have similarities with the structure of (acetylaceton)mono(*o*-hydroxyanil)copper(II) (Barclay & Hoskins, 1965).



The coordination around copper is distorted square planar, with bond angles ranging between 76.5 (3) and 98.0 (3)° (Fig. 1). The average Cu—O distance in the coordination square is 1.931 (9) Å and the Cu—N distance is 1.920 (10) Å. The Cu atom is located 0.021 (1) Å from the coordination best plane. Due to the centre of inversion at its centre, the Cu—O—Cu—O bridging plane moiety is planar, with Cu—O bond lengths of 1.930 (10) and 1.982 (9) Å. The bond angles within the bridging planes, Cu—O2—Cu<sup>i</sup> and O2—Cu—O2<sup>i</sup>, are 103.5 (4) and 76.5 (3)°, respectively [symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ ]. The bridging plane and the coordination square around copper have a dihedral angle of 11.3 (8)° between them. The Cu···Cu<sup>i</sup>

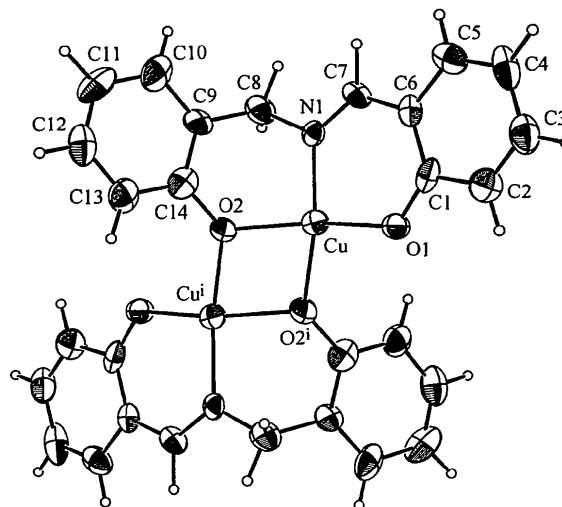


Fig. 1. ORTEPII (Johnson, 1976) drawing of  $[\text{Cu}_2(\text{C}_{14}\text{H}_{11}\text{NO}_2)_2]$  with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.