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Bis(pyridine-2,6-dimethanol-*N*,*O*,*O*′)-cobalt(II) and -copper(II) disaccharinate dihydrate: three-dimensional structures with extensive hydrogen bonds and aromatic *π*–*π*-stacking interactions

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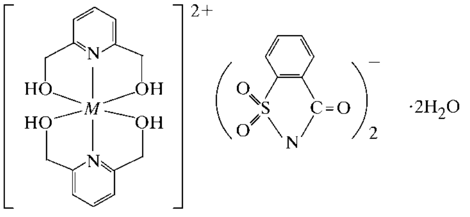
Bis(pyridine-2,6-dimethanol-*N*,*O*,*O*′)cobalt(II) disaccharinate dihydrate, $[Co(C_7H_9NO_2)_2](C_7H_4NO_3S)_2\cdot 2H_2O$, (I), and bis(pyridine-2,6-dimethanol-*N*,*O*,*O*′)copper(II) disaccharinate dihydrate, $[Cu(C_7H_9NO_2)_2](C_7H_4NO_3S)_2\cdot 2H_2O$, (II), collectively $[M(\text{dmpy})_2](\text{sac})_2\cdot 2H_2O$ (where *M* is Co^{II} or Cu^{II}, sac is the saccharinate anion and dmpy is pyridine-2,6-dimethanol), are isostructural. The $[M(\text{dmpy})_2]^{2+}$ cations exhibit distorted octahedral geometry in which the two neutral dmpy species act as tripodal *N*,*O*,*O*′-tridentate ligands. The crystal packing is determined by hydrogen bonding, as well as by weak pyridine–saccharinate *π*–*π*-stacking interactions.

Comment

The artificial sweetener saccharin (also known as 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide or *o*-benzosulfimide) is readily deprotonated to form the corresponding saccharinate anion (sac). The coordination behaviour of sac to metal ions depends on the presence of other co-ligands. Bulky ligands, such as 1,10-phenathroline (phen; Deng *et al.*, 2000, 2001; Williams *et al.*, 2000; Yilmaz *et al.*, 2001) and triethanolamine (tea; Topcu *et al.*, 2002; Andac *et al.*, 2001), prevent the coordination of sac to metal ions and so sac is present as a counter-ion in such complexes. The present study is part of our continuing research into the preparation and characterization of a series of mixed-ligand complexes of sac with N and O donor ligands and we report here the crystal structures of the pyridine-2,6-dimethanol (dmpy) complexes with cobalt and copper saccharinates, *viz.* $[Co(\text{dmpy})_2](\text{sac})_2\cdot 2H_2O$, (I), and $[Cu(\text{dmpy})_2](\text{sac})_2\cdot 2H_2O$, (II).



(I) $M = Co^{II}$
(II) $M = Cu^{II}$

The structures of (I) and (II) are shown in Figs. 1 and 2, respectively. Tables 1–4 list selected geometrical and hydrogen-bonding data. These isostructural phases consist of a complex cation, two sac ions and two lattice water molecules. In the complex cations, the Co^{II} or Cu^{II} ions are octahedrally coordinated by a pair of neutral dmpy ligands with no sac in the primary coordination sphere. Each dmpy ligand behaves as a tridentate ligand using all donor atoms, *i.e.* the amino N atom and both hydroxyl O atoms, and forms two five-membered metallocyclic chelate rings. The *M*—N bond lengths of the Co^{II} complex, (I), are noticeably longer than those of the Cu^{II} complex, (II), while the *M*—O bond distances of (I) are somewhat shorter than those of (II).

The *M*—N bond distances in (II) are somewhat longer than those found in $[Cu(\text{dmpy})_2](\text{nif})_2$, where nif is the niflumate anion (Koman & Melnik, 1997), and similar to the corresponding distances in [Cu(pydca)(dmpy)], where pydca is pyridine-2,6-dicarboxylate (Koman *et al.*, 2000), while the *M*—

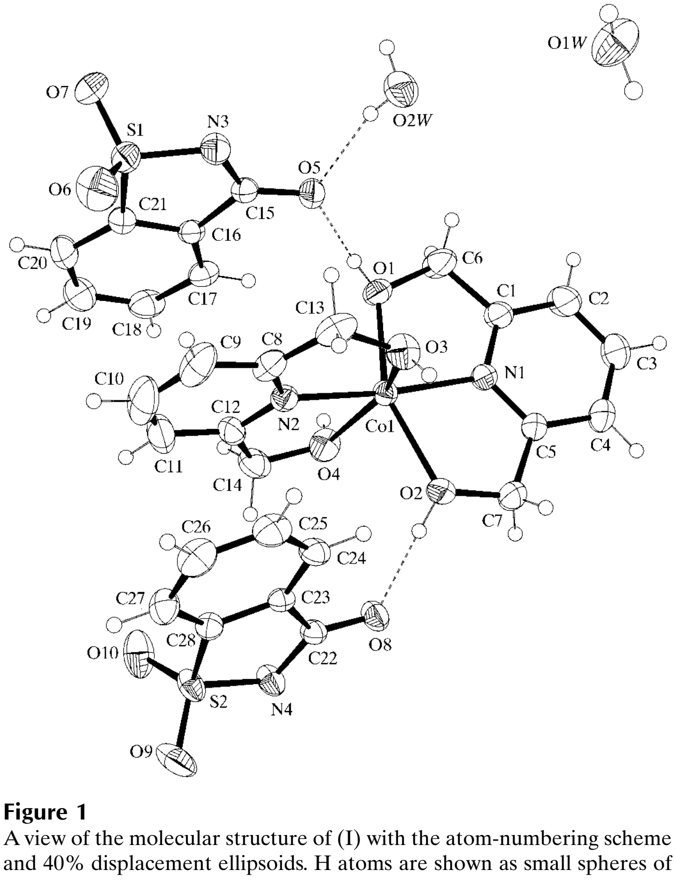


Figure 1
A view of the molecular structure of (I) with the atom-numbering scheme and 40% displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

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O bond distances are comparable with those observed in [Cu(dmpy)$_2$](nif)$_2$ and shorter than those found in [Cu(pydca)(dmpy)]. The larger deviations from regular octahedral geometry for the Cu phase are characteristic of the Jahn–Teller effect. The four *M*—O bonds forming the plane of the *M*O$_4$N$_2$ core are longer than the two *M*—N bonds occupying the axial positions, resulting in a 'compressed' distorted octahedron around the metal ions.

Both dmpy ligands are essentially planar, with an average r.m.s. deviation of 0.057 Å in (I) and 0.065 Å in (II). Both hydroxyl O atoms deviate slightly from the dmpy planes. The planes of the two dmpy ligands are nearly perpendicular to each other, and the dihedral angles between the corresponding planes are 83.73 (3)° for both (I) and (II). The sac anions are also planar, with average r.m.s. deviations of 0.029 and 0.031 Å for (I) and (II), respectively.

In both complexes, the sac ions adopt a parallel alignment with each other and the dihedral angles between the corresponding planes are 16.02 (5) and 13.95 (6)° for (I) and (II), respectively. One of the pyridine rings (ring *A* = N2/C8–C12) is located between the phenyl rings (ring *B* = C16–C21 and ring *C* = C23–C28) of the two sac ions. The planes of rings *A*, *B* and *C* also adopt a parallel alignment and the dihedral angles between *A* and *B*, and between *A* and *C* are 6.92 (12) and 11.39 (11)°, respectively, for (I), and 6.59 (14) and 9.36 (13)°, respectively, for (II). Additionally, the angle of the line passing through the centres of *C*–*A*–*B* to the plane of *A* is 159.86° for both complexes. As a result, the phenyl rings of the sac ions and pyridine rings are connected by weak π–π interactions: $A\cdots B$ 3.6349 (11) and $A\cdots C$ 3.6093 (11) Å for (I), and $A\cdots B$ 3.6299 (13) and $A\cdots C$ 3.5844 (12) Å for (II).

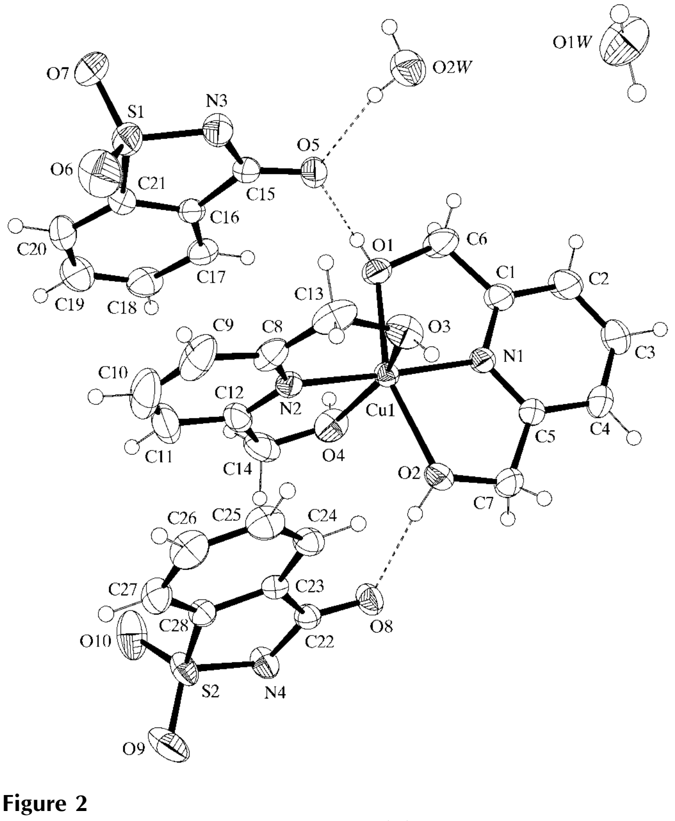

Figure 2
A view of the molecular structure of (II) with the atom-numbering scheme and 40% displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

The crystals exhibit a number of hydrogen bonds (Fig. 3). The packing and hydrogen-bonding schemes of compounds (I) and (II) are very similar. The H atoms of the hydroxyl groups of the dmpy ligands are involved in intermolecular hydrogen bonding with the water molecules and the carbonyl O atoms of neighbouring sac ions, while the H atoms of the two water molecules form bifurcated hydrogen bonds with the negatively charged amine N atom and carbonyl and sulfonyl O atoms of the sac ions. Additionally, there are weak C—H$\cdots$O interactions between phenyl H atoms and hydroxyl and sulfonyl O atoms. The crystal structures are stabilized by an infinite three-dimensional network of extensive hydrogen bonds and other intermolecular interactions.

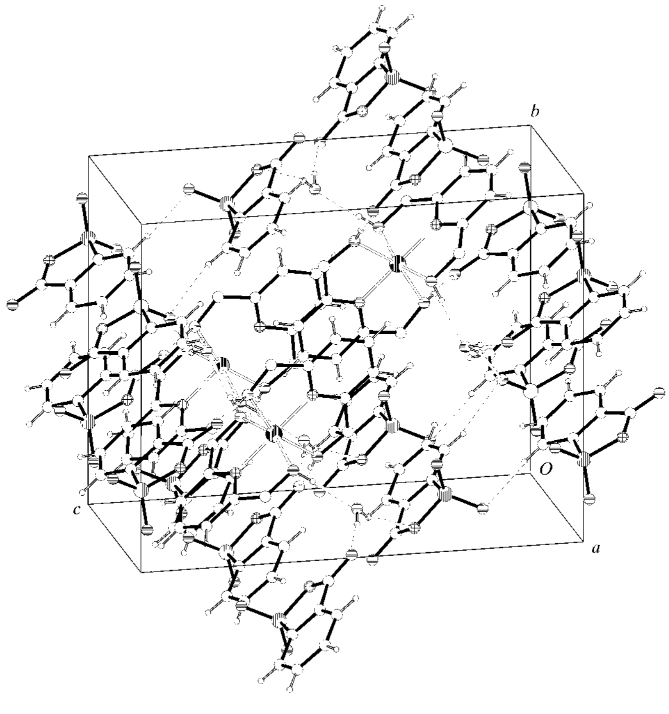

Figure 3
A packing diagram for (II).

Experimental

Previously prepared tetraaquabis(saccharinato)cobalt(II) and copper(II) dihydrates, [M(H$_2$O)$_4$(sac)$_2$]·2H$_2$O (1 mmol), were dissolved in a mixture of methanol–2-propanol (1:1 *v*:*v*; 30 ml) and mixed with the dmpy ligand (2 mmol) dissolved in methanol (15 ml) at room temperature. The resulting solutions were left to stand at room temperature and allowed to evaporate slowly over a period of a few days for crystallization. Crystals of (I) and (II) suitable for X-ray diffraction analysis were collected by suction filtration, washed with acetone and dried in air.

Compound (I)

Crystal data

$[\mathrm{Co(C_7H_9NO_2)_2}](\mathrm{C_7H_4NO_3S})_2\cdot 2\mathrm{H_2O}$
$M_r = 737.61$
Triclinic, $P\overline{1}$
$a = 8.1365\ (4)$ Å
$b = 12.5177\ (6)$ Å
$c = 15.7558\ (8)$ Å
$\alpha = 93.0540\ (10)^\circ$
$\beta = 97.4940\ (10)^\circ$
$\gamma = 98.0300\ (10)^\circ$
$V = 1571.24\ (13)$ Å^3
$Z = 2$
$D_x = 1.559$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4198 reflections
$\theta = 2.7$–29.9°
$\mu = 0.75$ mm^{-1}
$T = 298\ (2)$ K
Block, pale purple
$0.46 \times 0.42 \times 0.21$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.716$, $T_{\max} = 0.854$
19 456 measured reflections
9108 independent reflections
6843 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 30^\circ$
$h = -11 \rightarrow 10$
$k = -17 \rightarrow 17$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.094$
$S = 1.00$
9108 reflections
448 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}

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

Co1—N2	2.0341 (12)	Co1—O3	2.1295 (13)
Co1—N1	2.0385 (12)	Co1—O2	2.1334 (12)
Co1—O1	2.1086 (12)	Co1—O4	2.1455 (13)
N2—Co1—N1	173.86 (5)	O1—Co1—O2	153.14 (4)
N2—Co1—O1	98.82 (5)	O3—Co1—O2	91.06 (5)
N1—Co1—O1	76.85 (5)	N2—Co1—O4	76.86 (5)
N2—Co1—O3	76.87 (5)	N1—Co1—O4	107.66 (5)
N1—Co1—O3	99.01 (5)	O1—Co1—O4	95.02 (5)
O1—Co1—O3	95.06 (5)	O3—Co1—O4	152.99 (5)
N2—Co1—O2	108.04 (5)	O2—Co1—O4	91.15 (5)
N1—Co1—O2	76.36 (5)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O5	0.846 (16)	1.722 (16)	2.5658 (17)	175 (2)
O2—H2⋯O8	0.835 (15)	1.786 (16)	2.6192 (16)	176 (2)
O3—H3⋯O1$W^{\rm i}$	0.808 (16)	1.826 (17)	2.613 (2)	164 (3)
O4—H4⋯O2$W^{\rm i}$	0.812 (16)	1.835 (17)	2.620 (2)	162 (3)
O1W—H2W1⋯O8$^{\rm ii}$	0.821 (16)	1.997 (17)	2.8064 (18)	168 (3)
O1W—H1W1⋯N4$^{\rm iii}$	0.793 (16)	2.250 (17)	3.027 (2)	166 (3)
O2W—H2W2⋯O5	0.802 (16)	2.002 (16)	2.7861 (18)	166 (3)
O2W—H1W2⋯O7$^{\rm iv}$	0.805 (16)	2.086 (17)	2.877 (2)	168 (3)
C17—H17⋯O1	0.93	2.59	3.357 (2)	140
C20—H20⋯O10$^{\rm v}$	0.93	2.55	3.294 (2)	137
C27—H27⋯O7$^{\rm vi}$	0.93	2.58	3.341 (2)	139

Symmetry codes: (i) $x-1, y, z$; (ii) $2+x, y, z$; (iii) $-x, -y, 1-z$; (iv) $1-x, 1-y, 2-z$; (v) $-1-x, -y, 2-z$; (vi) $-x, -y, 2-z$.

Compound (II)

Crystal data

$[\mathrm{Cu(C_7H_9NO_2)_2}](\mathrm{C_7H_4NO_3S})_2\cdot 2\mathrm{H_2O}$
$M_r = 742.22$
Triclinic, $P\overline{1}$
$a = 8.1544\ (4)$ Å
$b = 12.4805\ (5)$ Å
$c = 15.7510\ (7)$ Å
$\alpha = 93.1950\ (10)^\circ$
$\beta = 97.5010\ (10)^\circ$
$\gamma = 97.8770\ (10)^\circ$
$V = 1569.85\ (12)$ Å^3
$Z = 2$
$D_x = 1.570$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5581 reflections
$\theta = 2.2$–29.3°
$\mu = 0.90$ mm^{-1}
$T = 298\ (2)$ K
Rod, blue
$0.52 \times 0.30 \times 0.19$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.731$, $T_{\max} = 0.843$
13 441 measured reflections
8915 independent reflections
6477 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 30^\circ$
$h = -8 \rightarrow 11$
$k = -17 \rightarrow 16$
$l = -22 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.090$
$S = 0.94$
8915 reflections
448 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

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

Cu1—N1	1.9455 (14)	Cu1—O2	2.1603 (14)
Cu1—N2	1.9432 (15)	Cu1—O3	2.1806 (14)
Cu1—O1	2.1168 (13)	Cu1—O4	2.1809 (15)
N2—Cu1—N1	176.96 (6)	O1—Cu1—O3	93.62 (6)
N2—Cu1—O1	99.30 (6)	O2—Cu1—O3	90.16 (6)
N1—Cu1—O1	79.10 (6)	N2—Cu1—O4	78.92 (6)
N2—Cu1—O2	103.30 (5)	N1—Cu1—O4	103.70 (6)
N1—Cu1—O2	78.30 (5)	O1—Cu1—O4	93.78 (6)
O1—Cu1—O2	157.40 (5)	O2—Cu1—O4	91.22 (6)
N2—Cu1—O3	78.66 (6)	O3—Cu1—O4	157.25 (6)
N1—Cu1—O3	98.82 (6)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O5	0.819 (16)	1.745 (16)	2.5639 (18)	179 (3)
O2—H2⋯O8	0.812 (16)	1.820 (16)	2.6267 (18)	173 (3)
O3—H3⋯O1$W^{\rm i}$	0.797 (16)	1.842 (17)	2.631 (2)	171 (3)
O4—H4⋯O2$W^{\rm i}$	0.788 (16)	1.873 (18)	2.629 (2)	160 (3)
O1W—H1W1⋯O8$^{\rm ii}$	0.796 (16)	2.041 (17)	2.825 (2)	168 (3)
O1W—H2W1⋯N4$^{\rm iii}$	0.801 (17)	2.284 (19)	3.052 (2)	161 (3)
O2W—H1W2⋯O5	0.818 (17)	1.985 (17)	2.791 (2)	169 (3)
O2W—H2W2⋯O7$^{\rm iv}$	0.809 (17)	2.084 (18)	2.858 (2)	160 (3)
C17—H17⋯O1	0.93	2.56	3.324 (2)	139
C20—H20⋯O10$^{\rm v}$	0.93	2.53	3.289 (3)	139
C27—H27⋯O7$^{\rm vi}$	0.93	2.56	3.296 (2)	136

Symmetry codes: (i) $x-1, y, z$; (ii) $2+x, y, z$; (iii) $-x, -y, 1-z$; (iv) $1-x, 1-y, 2-z$; (v) $-1-x, -y, 2-z$; (vi) $-x, -y, 2-z$.

Hydroxyl and water H atoms were found in difference maps and were positionally refined with geometric restraints (O—H = 0.82 Å for both hydroxyl and water H atoms, and H···H = 1.30 Å for the water H atoms) and with $U_{iso}(H) = 1.5U_{eq}$ of the parent atom. The remaining H atoms were placed in calculated positions 0.93 Å from their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1148). Services for accessing these data are described at the back of the journal.

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