Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Two saccharinate complexes: $[Mn(phen)_2(sac)(H_2O)]^+\cdot sac^-$ and $[Co(bipy)_2(sac)(H_2O)]^+\cdot sac^-$

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Received 6 July 1999
Accepted 5 October 1999

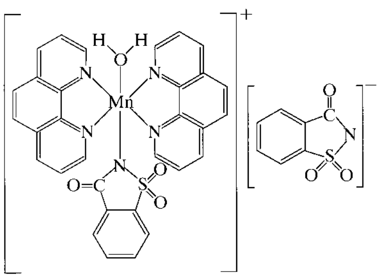
The title saccharinate complexes, aqua[1,2-benzisothiazol-3(2*H*)-onato 1,1-dioxide-*N*]bis(1,10-phenanthroline-*N*,*N*′)manganese(II) 1,2-benzisothiazol-3(2*H*)-onate 1,1-dioxide, $[Mn(C_7H_4NO_3S)(C_{12}H_8N_2)_2(H_2O)](C_7H_4NO_3S)$, and aqua[1,2-benzisothiazol-3(2*H*)-onato 1,1-dioxide-*N*]bis(2,2′-bipyridine-*N*,*N*′)cobalt(II) 1,2-benzisothiazol-3(2*H*)-onate 1,1-dioxide, $[Co(C_7H_4NO_3S)(C_{10}H_8N_2)_2(H_2O)](C_7H_4NO_3S)$, have been prepared and their crystal structures determined at 150 K. The structure of the manganese complex consists of repeated alternating $[Mn(phen)_2(sac)(H_2O)]^+$ cations and non-coordinated saccharinate anions. The water molecule, bound to manganese as part of a slightly distorted octahedral arrangement, is hydrogen bonded to an O atom of the SO_2 group in the saccharinate counter-ion. In contrast, the cobalt complex has one pseudo-octahedral $[Co(bipy)_2(sac)(H_2O)]^+$ cation, with the cobalt-bound water molecule hydrogen bonded to the N atom of the accompanying free saccharinate anion.

Comment

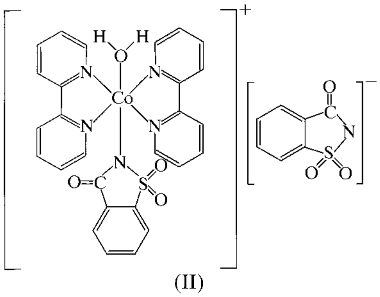
In an earlier paper (Dillon *et al.*, 1999), we summarized previous work on the crystal structures of transition metal–1,2-benzisothiazol-3(2*H*)-onate 1,1-dioxide (saccharinate) complexes, particularly those with the bidentate ligands 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) present. These included examples with all the saccharinate ligands attached to the metal (Hergol-Brundic *et al.*, 1989), ones where saccharinate is present merely as the counter-ion (Ainscough *et al.*, 1990; Li, Chen *et al.*, 1993; Li, Wei *et al.*, 1993), and, for some copper complexes only, where it occurs in both the cation and the anion (Li *et al.*, 1991; Hergold-Brundic *et al.*, 1991; Zhang *et al.*, 1994). We described previously the first structure of a manganese(II) complex with saccharinate present in both the cation and anion (Dillon *et al.*, 1999).

The synthesis and crystal structures are now reported of two further saccharinate complexes with saccharinate (sac) present both in the cation and as the counter-ion, namely $[Mn(phen)_2(sac)(H_2O)]^+\cdot sac^-$, (I), and $[Co(bipy)_2(sac)(H_2O)]^+\cdot sac^-$, (II), the latter representing the first cobalt(II) example of this kind of structure.

The structures of (I) (Fig. 1) and (II) (Fig. 2) both consist of polymeric cation chains composed of $[Mn(phen)_2(sac)(H_2O)]^+$ and $[Co(bipy)_2(sac)(H_2O)]^+$ units, respectively, and saccharinate counter-ions. Within the cation of (I), the mean Mn—N_{phen} bond length is 2.257 (6) Å, with one of the phen ligands (N2/N3) bound more asymmetrically than the other, as was also found in the structure of $[Mn(bipy)_2(sac)(H_2O)]^+$ (Dillon *et al.*, 1999). The Mn—N_{sac} bond length of 2.225 (2) Å is close to that in the bipy complex and may be compared with the corresponding distance of 2.281 (1) Å in $[Mn(sac)_2(H_2O)_4]\cdot 2H_2O$ (Kamenar & Jovanovski, 1982). The Mn—O_{aqua} separation of 2.189 (2) Å is rather longer than in the bipy complex [2.127 (3) Å], possibly reflecting the greater steric requirements of the phen ligand, and is intermediate between the two independent Mn—O_{aqua} distances of 2.162 (1) and 2.219 (2) Å in $[Mn(sac)_2(H_2O)_4]\cdot 2H_2O$ (Kamenar & Jovanovski, 1982). Bond angles about manganese show even greater distortion from idealized octahedral geometry than in the bipy complex (Dillon *et al.*, 1999), with N2—Mn—N5 = 176.09 (6)°, O4—Mn—N3 = 159.10 (6)° and N1—Mn—N4 = 163.53 (6)°. This result is again not unexpected for the more sterically demanding phen ligand. An interesting difference from the structure of the bipy complex is that the water molecule attached to manganese is hydrogen bonded to an O atom of the SO_2 group in the free saccharinate anion (Fig. 1), with an H···O7 distance of 1.91 (3) Å; in the former, the water is hydrogen bonded to the N atom in the counter-ion.



(I)



(II)

As expected, the corresponding bond lengths in the cobalt complex, (II), are shorter than those in (I) just as in the saccharinate species $[M(sac)_2(H_2O)_4]\cdot 2H_2O$ [M = Mn (Kamenar & Jovanovski, 1982) and Co (Haider *et al.*, 1983)]. The average Co—N_{bipy} bond length is 2.144 (4) Å, though the ligand asymmetry seen in compound (I) is not displayed. The Co—N$_{sac}$ distance of 2.169 (2) Å compares well with the distance of 2.200 (1) Å in [Co(sac)$_2$(H$_2$O)$_4$]·2H$_2$O (Haider *et al.*, 1983), while the Co—O$_{aqua}$ distance of 2.057 (2) Å in (II) is similar to the shorter of the two independent Co—O$_{aqua}$ bond lengths of 2.060 (1) and 2.124 (2) Å in [Co(sac)$_2$(H$_2$O)$_4$]·2H$_2$O. Some distortion of regular geometry is apparent in the cation [O4—Co1—N2 = 165.61 (6)°, N3—Co1—N4 = 174.59 (6)° and N5—Co1—N1 = 170.83 (6)°], though this is less pronounced than in the manganese compound (I), again showing the sterically less demanding

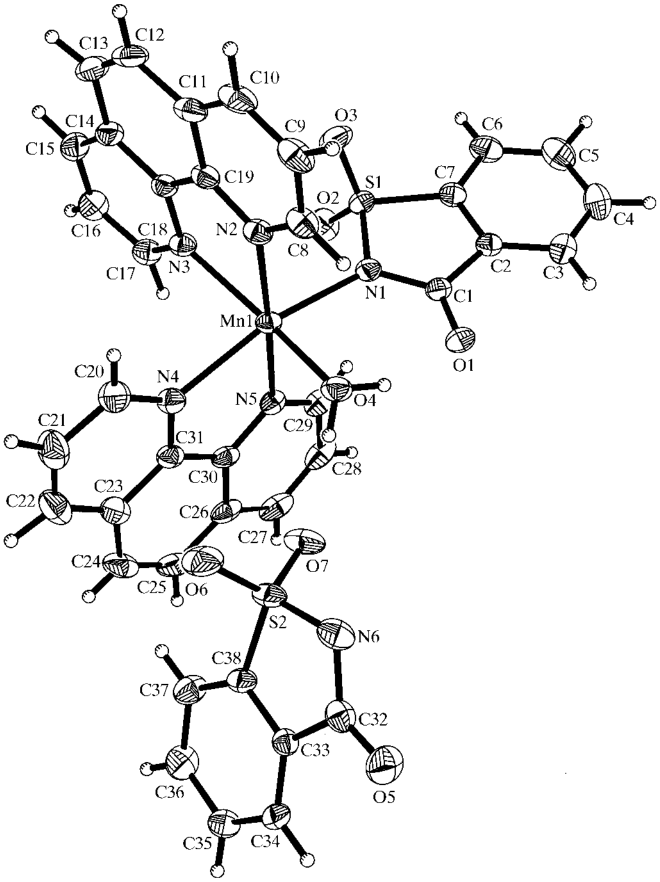


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

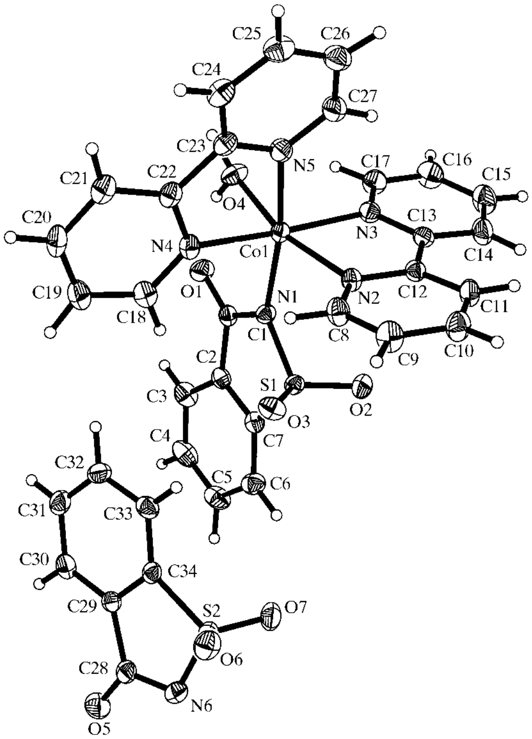


Figure 2
The molecular structure of (II) showing 50% probability displacement ellipsoids.

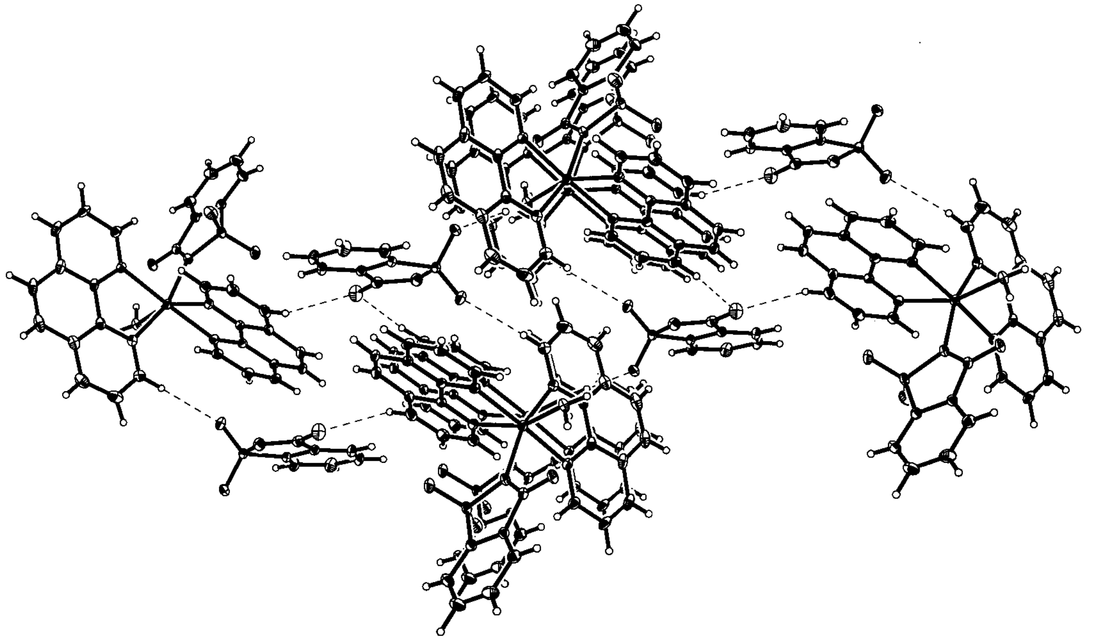


Figure 3
Packing diagram of (I) with intermolecular contacts indicated by dotted lines.

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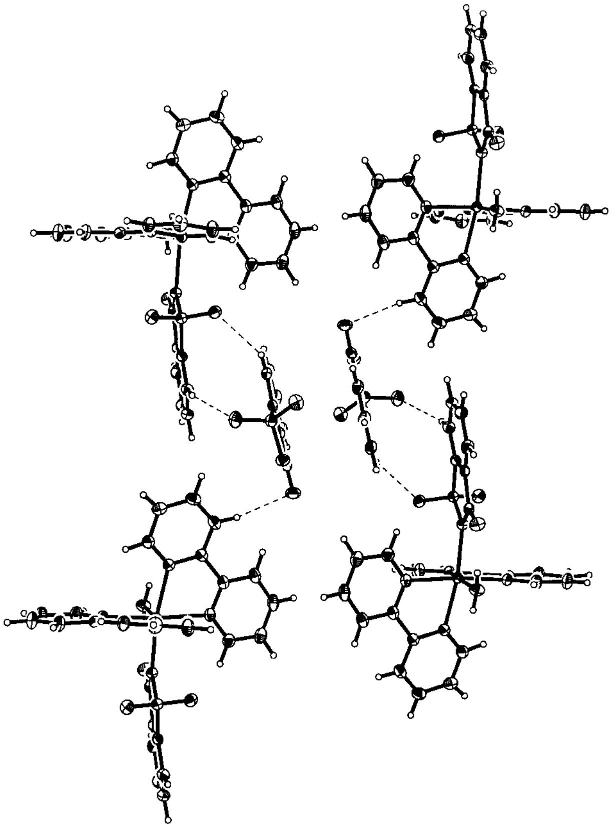

Figure 4
Packing diagram of (II); note the free and bound saccharinate groups alternating in a staggered conformation.

nature of the bipy ligand compared with phen. The water molecule in (II) is hydrogen bonded to the N6 atom in the adjacent free saccharinate ion, at an H···O distance of 1.78 (3) Å, as in the structure of [Mn(sac)(bipy)$_2$(H$_2$O)](sac) (Dillon *et al.*, 1999). The structural parameters for the free anions in both (I) and (II) are again very similar to those in K$_2$Na(sac)$_3$·H$_2$O (Malik *et al.*, 1984).

The packing of compound (I) involves parallel stacking of pairs of phen ligands, as shown in Fig. 3. The structure demonstrates two significant intermolecular contacts. In addition to the hydrogen bond between O7 in the SO$_2$ group and the bound water molecule mentioned above, a phenyl H atom from the phenanthroline ligand (H20), which stacks in a pairwise fashion, also forms a close contact with O6^{i} at a distance of 2.50 (2) Å [symmetry code: (i) $-x, 1-y, 1-z$]. The three-dimensional arrangement of compound (II) is very similar to that of the manganese analogue reported previously (Dillon *et al.*, 1999). The free and bound saccharinate groups alternate in a staggered conformation, as shown in Fig. 4. The pairs of sac ligands are linked by close intermolecular contacts of 2.50 (3) Å for C6—H6···O7═S2 and 2.56 (2) Å for C33—H33···O3═S1. There is also a close contact of 2.49 (3) Å between C20—H20 and O1^{ii}═C1^{ii}, as well as a linear hydrogen bond of 1.78 (3) Å between H4*B* and N6^{iii} with an O—H···N angle of 174.0 (3)° [symmetry codes: (ii) $2-x, -y, 1-z$; (iii) $x, y, z-1$].

Experimental

Compound (I) was prepared by adding with stirring a warm solution of 1,10-phenanthroline (0.1546 g, 0.78 mmol) in water (50 ml) to a warm clear solution of [Mn(sac)$_2$(H$_2$O)$_4$]·2H$_2$O (0.2100 g, 0.39 mmol) in water (50 ml). The resulting yellow solution was warmed on a hot-plate with stirring and the volume reduced to 25 ml. The bright yellow solution was allowed to stand overnight and yellow crystals were deposited. These were collected by filtration, washed with three 5 ml portions of cold water and dried over silica gel [yield 0.1213 g (75.8%), m.p. 485 K]. Elemental analyses, including Mn and Co by atomic absorption, were performed by the microanalytical services of the Department of Chemistry, University of Durham; found: C 57.29, H 3.18, N 10.38, Mn 6.22%; C$_{38}$H$_{26}$MnN$_6$O$_7$S$_2$ requires: C 57.22, H 3.29, N 10.54, Mn 6.89%. Compound (II) was prepared by adding with stirring a warm solution of 2,2′-bipyridine (0.1176 g, 0.75 mmol) in water (25 ml) to a warm solution of [Co(sac)$_2$(H$_2$O)$_4$]·2H$_2$O (0.2002 g, 0.38 mmol) in water (25 ml). The resulting intense yellow solution was warmed on a hot-plate with stirring and the volume reduced to 20 ml. The brown solution was allowed to stand overnight and bright orange crystals of the compound were then isolated [yield 0.2110 g (75.9%), m.p. 455 K]. Found: C 53.71, H 3.36, N 10.97, Co 7.90%; C$_{34}$H$_{26}$CoN$_6$O$_7$S$_2$ requires: C 54.18, H 3.48, N 11.15, Co 7.82%.

Compound (I)

Crystal data

[Mn(C$_7$H$_4$NO$_3$S)(C$_{12}$H$_8$N$_2$)$_2$-(H$_2$O)](C$_7$H$_4$NO$_3$S)
M_r = 797.71
Triclinic, $P\bar{1}$
a = 7.943 (2) Å
b = 14.448 (3) Å
c = 15.336 (3) Å
α = 99.01 (3)°
β = 96.19 (3)°
γ = 91.54 (3)°
V = 1726.3 (6) Å^3
Z = 2
D_x = 1.535 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 998 reflections
θ = 10.25–27.34°
μ = 0.566 mm^{-1}
T = 150 K
Block, yellow
0.45 × 0.25 × 0.10 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.773, $T_{\max}$ = 0.945
13 847 measured reflections
8956 independent reflections
6420 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.023
$\theta_{\max}$ = 30.35°
$h = -11 \rightarrow 10$
$k = -20 \rightarrow 17$
$l = -21 \rightarrow 19$

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

Mn1—N1	2.2253 (18)	N1—C1	1.354 (3)
Mn1—N2	2.2382 (17)	N1—S1	1.6461 (17)
Mn1—N3	2.2542 (18)	N6—C32	1.370 (3)
Mn1—N4	2.2678 (19)	N6—S2	1.598 (2)
Mn1—N5	2.2678 (17)	O4—H4*A*	0.89 (3)
Mn1—O4	2.1897 (17)	O4—H4*B*	0.83 (3)
N1—Mn1—N2	90.86 (6)	N3—Mn1—N5	101.68 (6)
N1—Mn1—N3	100.84 (6)	N3—Mn1—O4	159.10 (6)
N1—Mn1—N4	163.53 (6)	N4—Mn1—N5	73.82 (7)
N1—Mn1—N5	89.81 (7)	N4—Mn1—O4	89.51 (7)
N1—Mn1—O4	90.41 (7)	O4—Mn1—N5	95.86 (7)
N2—Mn1—N3	74.42 (7)	C1—N1—S1	111.76 (14)
N2—Mn1—N4	105.59 (7)	C32—N6—S2	111.59 (15)
N2—Mn1—N5	176.09 (6)	Mn1—O4—H4*A*	107 (2)
N2—Mn1—O4	87.98 (7)	Mn1—O4—H4*B*	124 (2)
N3—Mn1—N4	84.61 (6)		

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.095$
$S = 1.008$
8956 reflections
591 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Compound (II)

Crystal data

$[Co(C_7H_4NO_3S)(C_{10}H_8N_2)_2(H_2O)](C_7H_4NO_3S)$
$M_r = 753.66$
Monoclinic, $P2_1/n$
$a = 7.6982$ (1) Å
$b = 31.3359$ (5) Å
$c = 13.2179$ (2) Å
$\beta = 93.272$ (1)°
$V = 3183.36$ (8) Å^3
$Z = 4$

$D_x = 1.573$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 501 reflections
$\theta = 14.87$–19.99°
$\mu = 0.732$ mm^{-1}
$T = 150$ K
Block, orange
0.4 × 0.3 × 0.3 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.651$, $T_{\max} = 0.803$
22 343 measured reflections

7238 independent reflections
6294 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 27.46$°
$h = -9 \rightarrow 9$
$k = -40 \rightarrow 40$
$l = -17 \rightarrow 12$

Refinement

Refinement on F^2
$R(F) = 0.033$
$wR(F^2) = 0.079$
$S = 1.147$
7238 reflections
555 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2 + 2.8879P]$
where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}

All H atoms were refined and the C—H distances are in the ranges 0.83 (3)–1.03 (3) and 0.90 (3)–0.99 (3) Å for (I) and (II), respectively.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); 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: *SHELXTL* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97.

JAKH thanks the University of Durham for a Sir Derman Christopherson Foundation Fellowship and CB thanks the EPSRC for financial support.

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

Co1—N1	2.1688 (17)	N1—C1	1.366 (2)
Co1—N2	2.1339 (16)	N1—S1	1.6465 (16)
Co1—N3	2.1482 (16)	N6—C28	1.364 (3)
Co1—N4	2.1516 (16)	N6—S2	1.6180 (18)
Co1—N5	2.1403 (17)	O4—H4*A*	0.81 (3)
Co1—O4	2.0565 (15)	O4—H4*B*	0.95 (3)
N1—Co1—N2	95.21 (6)	N3—Co1—N4	174.59 (6)
N1—Co1—N3	91.02 (6)	N3—Co1—N5	98.11 (6)
N1—Co1—N4	94.10 (6)	N3—Co1—O4	90.14 (6)
N1—Co1—N5	170.83 (6)	N4—Co1—N5	76.75 (6)
N1—Co1—O4	90.50 (6)	N4—Co1—O4	91.54 (6)
N2—Co1—N3	76.58 (6)	N5—Co1—O4	90.30 (6)
N2—Co1—N4	101.19 (6)	C1—N1—S1	111.40 (13)
N2—Co1—N5	86.17 (6)	C28—N6—S2	112.20 (13)
N2—Co1—O4	165.61 (6)		

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1359). Services for accessing these data are described at the back of the journal.

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