Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

5-Aminonaphthalene-1-sulfonic acid and its manganese, nickel and cobalt salts

Dane J. Genther,[a] Philip J. Squattrito,[a]* Kristin Kirschbaum,[b] Eric J. Yearley[b] and A. Alan Pinkerton[b]

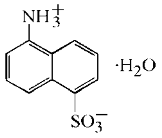
[a]Department of Chemistry, Central Michigan University, Mount Pleasant, MI 48859, USA, and [b]Department of Chemistry, University of Toledo, Toledo, OH 43606, USA
Correspondence e-mail: p.squattrito@cmich.edu

Received 11 October 2007
Accepted 21 October 2007
Online 24 November 2007

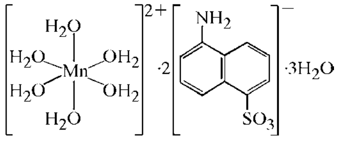
5-Ammonionaphthalene-1-sulfonate monohydrate, $C_{10}H_9NO_3S\cdot H_2O$, contains layers of zwitterionic molecules with the acidic sulfonic acid H atom transferred to the amine N atom. Within each layer, the charged groups (NH_3^+ and SO_3^-) are directed to the surface of the layer and are inverted on adjacent molecules. The naphthalene rings in a given layer are all parallel. The layers are held together by N—H···O and O—H···O hydrogen bonds involving the ammonium, sulfonate and water atoms. The Mn and Ni salts crystallize as fully aquated trihydrates, namely hexaaquamanagnese(II) bis(5-aminonaphthalene-1-sulfonate) trihydrate, $[Mn(H_2O)_6](C_{10}H_8NO_3S)_2\cdot 3H_2O$, (II), and hexaaquanickel(II) bis(5-aminonaphthalene-1-sulfonate) trihydrate, $[Ni(H_2O)_6](C_{10}H_8NO_3S)_2\cdot 3H_2O$, (III), in which layers of hexaaquametal(II) complexes alternate with layers of 5-aminonaphthalene-1-sulfonate anions. The cations reside on twofold rotation axes and display regular octahedral coordination. The additional water molecules are found in the inorganic layer between the complex cations, one on a twofold axis and one in a general position. The anions are packed in a herring-bone arrangement with the rings of neighboring rows of anions approximately 43° out of parallel. The NH_2 and SO_3^- groups line the surface of the layer, where they participate in numerous hydrogen bonds with the water molecules. Whereas the Mn and Ni salts are orthorhombic, the Co salt, hexaaquacobalt(II) bis(5-aminonaphthalene-1-sulfonate) dihydrate, $[Co(H_2O)_6](C_{10}H_8NO_3S)_2\cdot 2H_2O$, (IV), crystallizes in a triclinic cell of similar dimensions, with the cations situated on centers of inversion. The overall packing is very similar to that of the Mn and Ni salts, with the main differences being the absence of the solvent water molecule on the special position and subtle modifications in the positioning of the anions within their layers. This series of salts is compared with those of the same metals with the 5-aminonaphthalene-2-sulfonate and 4-aminonaphthalene-1-sulfonate isomers, allowing for similarities and differences in packing to be discussed on the basis of the differing substitution of the naphthalene ring and, in some cases, differing degrees of hydration.

Comment

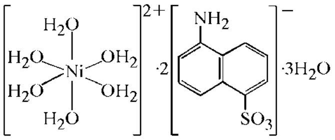
Mixed organic–inorganic structures have been of interest over the past three decades due to their potential as functional materials. One class of compounds that has received considerable attention is metal organophosphonate salts (Thompson, 1994; Clearfield, 1998). Metal organosulfonate salts have also been actively studied in recent years as part of the growing field of crystal engineering. Both similarities with and differences from the corresponding phosphonates have been found. Key results have been summarized in two recent reviews (Cote & Shimizu, 2003; Cai, 2004).



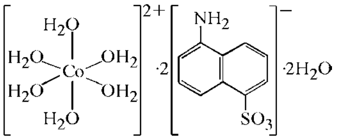
(I)



(II)



(III)



(IV)

We have previously characterized a variety of amine-substituted naphthalenesulfonate salts of main group and transition metals with the goal of discerning structural trends as functions of the metal cation and the substitution of the sulfonate group. Having examined structures containing 6-aminonaphthalene-2-sulfonate (Gunderman & Squattrito, 1995), 4-aminonaphthalene-1-sulfonate (Morris *et al.*, 2003) and 5-aminonaphthalene-2-sulfonate (Downer *et al.*, 2006), we now report the structures of a series of salts of 5-amino-

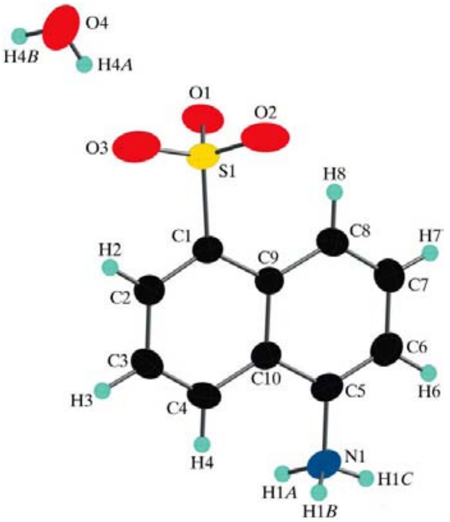


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

naphthalene-1-sulfonate, as well as the parent acid itself. These results are compared with those of the isomeric sulfonates.

5-Aminonaphthalene-1-sulfonic acid, (I), crystallizes as a monohydrate. The unit cell and space group have been reported previously (Corbridge *et al.*, 1966) but this is the first complete structure determination. As is typical for amine-substituted sulfonic acids (Gunderman & Squattrito, 1996; Leonard & Squattrito, 1997), the molecules exist in the zwitterionic ammoniosulfonate form, with the acidic H atom on the amine N atom (Fig. 1). The conformation of the sulfonate group has atom O3 essentially eclipsing the naphthalene ring system [O3—S1—C1—C2 torsion angle = 5.0 (2)°]. The molecules are packed in layers that stack along the *c* axis, with the charged groups directed to the surfaces of the layer (Fig. 2). The anions are positioned so that all the rings are parallel, with contacts between adjacent rings of *ca* 3.7 Å. Within each layer, rows of molecules have the sulfonate and ammonio groups alternating in opposite orientations along *b*. The packing is directed both within and between layers by four nearly linear hydrogen bonds involving the three ammonio H atoms (two to sulfonate O atoms and one to the water O atom) and one of the water H atoms to a sulfonate O atom (Table 1). The other water H atom is involved in a slightly weaker nonlinear interaction with a sulfonate O atom.

The manganese and nickel salts, (II) and (III), respectively, crystallize in the orthorhombic space group $P2_12_12$ with the formula $[M(H_2O)_6](H_2NC_{10}H_6SO_3)_2\cdot 3H_2O$ (M = Mn or Ni), consisting of hexaaquametal(II) cations, 5-aminonaphthalene-1-sulfonate anions and three water molecules of crystallization (Fig. 3). The two salts are isostructural and differ only in that the absolute structure refinements yield apparently opposite enantiomers. It is likely that we have both enantiomeric crystals in both products and that the selection was accidental. The presence of fully hydrated cations is typical of the behavior of divalent transition metals in these aminosulfonate systems, which are crystallized from aqueous solutions (Gunderman *et al.*, 1997). Only a few examples have been observed where either the N or O atoms of the sulfonate coordinate directly to the metal under these conditions (Gunderman *et al.*, 1996; Downer *et al.*, 2006). The cations reside on twofold rotation axes and display a modestly distorted octahedral geometry. The maximum deviations from ideal bond angles are in the range of 10–12° for Mn [O5—Mn1—O4 = 167.97 (3)° and O5—Mn1—O6^{i} = 99.39 (4)°; symmetry code: (i) $1 - x$, $2 - y$, z], while for Ni, all angles are within 5° of ideal. The sulfonate group displays the same eclipsed conformation as in the parent acid [O3—S1—C1—C2 torsion angle = −4.89 (9)° for (II) and 3.93 (16)° for (III)].

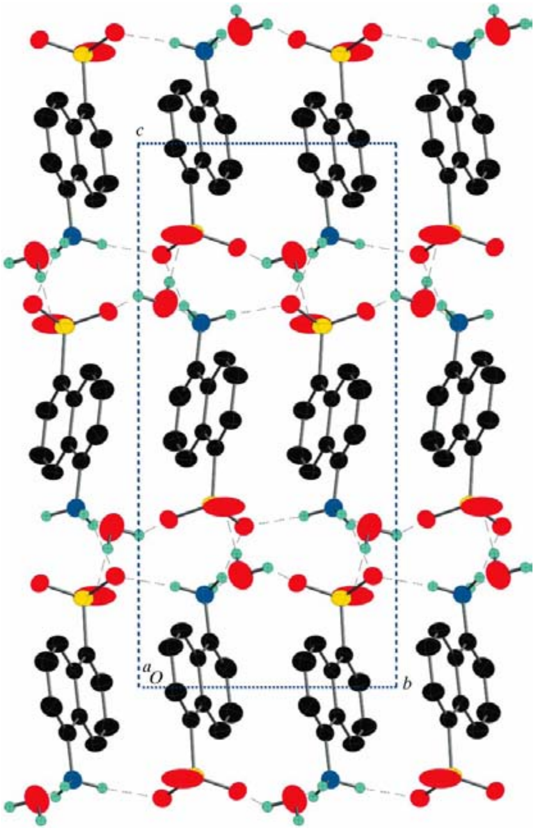


Figure 2
The packing of (I), viewed down the *a* axis, showing layers connected by O—H···O and N—H···O hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted.

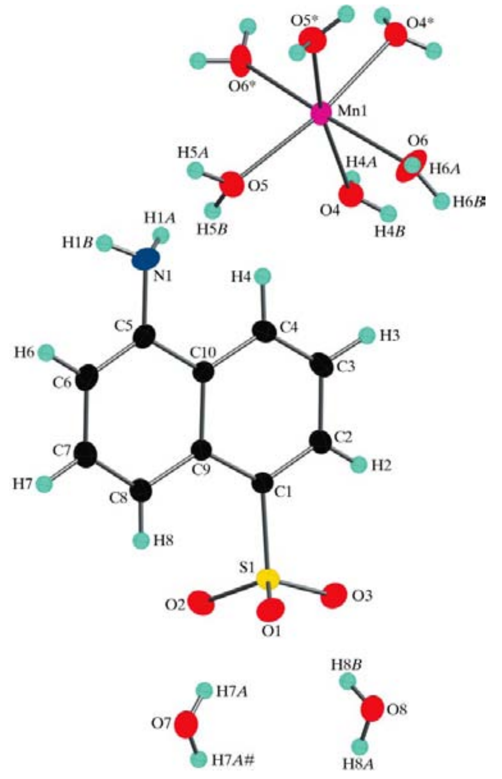


Figure 3
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry-equivalent water molecules (marked with an asterisk or a hash) are included to show the complete coordination environment of the cation. The Ni salt, (III), is isostructural with (II). [Symmetry codes: (*) $1 - x$, $2 - y$, z; (#) $1 - x$, $1 - y$, $-z$.]

The crystal packing (Fig. 4) is typical for transition metal arene- and naphthalenesulfonates (Chen *et al.*, 2002; Gunderman *et al.*, 1997), consisting of alternating layers of hexaaquametal cations and sulfonate anions parallel to the *ac* plane, with the anions positioned so that the polar and charged groups (*i.e.* NH_2 and SO_3^-) line the surface of the layer. Within each layer, alternating rows of molecules have the sulfonate and amino groups in opposite orientations and the rings canted in opposite directions (interplanar angle *ca* 43°) in a herring-bone arrangement. The solvent water molecules are located in between the cations in close association with the charged groups and coordinated water molecules, so as to participate in hydrogen-bonding interactions. One of the two crystallographically independent water molecules is located on a twofold rotation axis. The layers are held together by a series of robust (H$\cdots$*A* *ca* 2.0 Å) approximately linear O—H$\cdots$O and O—H$\cdots$N hydrogen bonds involving water donors and sulfonate, amine and water acceptors (Table 2). The amine H atoms participate in slightly longer hydrogen bonds (H$\cdots$O *ca* 2.3–2.4 Å) with sulfonate O atoms. The packing is comparable with that found in the Mn salt of 4-aminonaphthalene-1-sulfonate (Morris *et al.*, 2003), which has very similar cell dimensions and a herring-bone arrangement of the anions. This is not surprising given that both isomers have the polar/ionic groups perpendicular to the long dimension of the naphthalene ring system (*i.e.* in ring positions 1, 4, 5 or 8), and so would be similarly positioned to maximize favorable interactions with the cation layers. This is borne out by the very comparable distances between the metal atom layers, *ca* 11.4 Å for (II) and *ca* 11.7 Å for the 4,1 isomer. The structures do differ in degree of hydration, crystal system and space group (the 4,1 isomer crystallizes with two solvent water molecules per formula unit in the monoclinic space group $P2_1/c$). By contrast, the Mn salt of 5-aminonaphthalene-2-sulfonate (Downer *et al.*, 2006) has a very different packing, caused primarily by the positioning of the SO_3^- group on one of the terminal C atoms of the ring system (positions 2, 3, 6 and 7), which causes the anions to be situated in the layer with the long dimension of the ring system closer to perpendicular to the layer. This is reflected in the longer repeat distance between the layers (*ca* 14.2 Å). The spacing within the layers is also somewhat larger and the added voids between the metal complexes are occupied by water, as the 5,2 isomer has six solvent water molecules per formula unit. Although only alkali metal salts of 6-aminonaphthalene-2-sulfonate have been characterized to date (Gunderman & Squattrito, 1995),

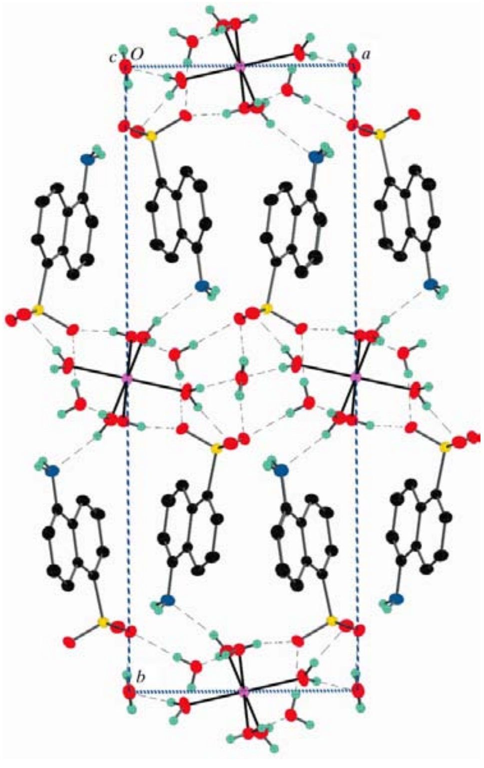


Figure 4
The packing of (II), viewed down the *c* axis, showing layers of hydrated cations and additional water molecules alternating with layers of anions and connected by O—H$\cdots$O and N—H$\cdots$O hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted.

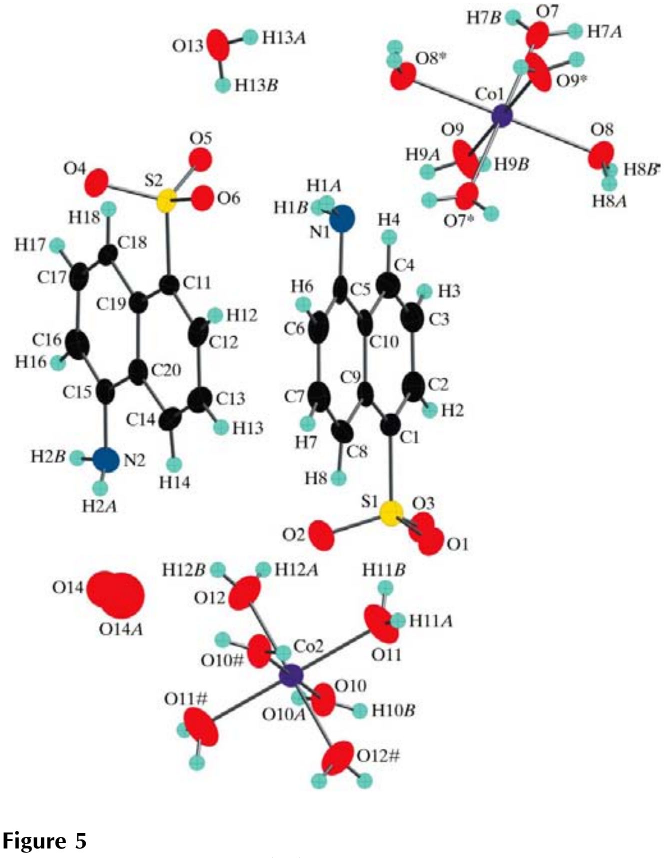


Figure 5
The molecular structure of (IV), showing two independent Co cations and sulfonate anions, along with two solvent water molecules. Additional symmetry-equivalent water molecules (marked with an asterisk or a hash) are included to show the complete coordination environments of the cations. One solvent water molecule is disordered over two nearby positions labeled O14 and O14*A*. The H atoms on this water molecule could not be located. [Symmetry codes: (*) $-x, -y, 1 - z$; (#) $-x, 1 - y, -z$.]

the anion packing follows the expected pattern. If fully hydrated transition metal salts of the 6,2 isomer were to be obtained, the interlayer repeat distance would be expected to be slightly larger than that of the 5,2 isomer.

Nickel shows somewhat greater variability in its behavior. The Ni salt of 4-aminonaphthalene-1-sulfonate (Morris *et al.*, 2003) crystallizes as a trihydrate like (III), but in an orthorhombic cell with both the *b* and *c* axes doubled. This unprecedented layered sulfonate structure contains a quadruple layer repeat pattern with two different types of sulfonate layer. Nevertheless, the layer thicknesses are very similar [*ca* 11.3 Å *versus ca* 11.5 Å for (III)], as is the case for the Mn salts. The Ni salt of 5-aminonaphthalene-2-sulfonate (Downer *et al.*, 2006) also has a completely different structure from the Mn (or Co) salt. In that compound, the Ni atom is coordinated by four water molecules and two sulfonate anions through the amine N atom, and it thus constitutes one of the rare examples of direct coordination involving the sulfonate anion with a transition metal ion. Due to the direct Ni—N bonding, the thickness of the layer (*ca* 11.5 Å) is less than the *ca* 14.2 Å dimension for the fully hydrated Mn salt.

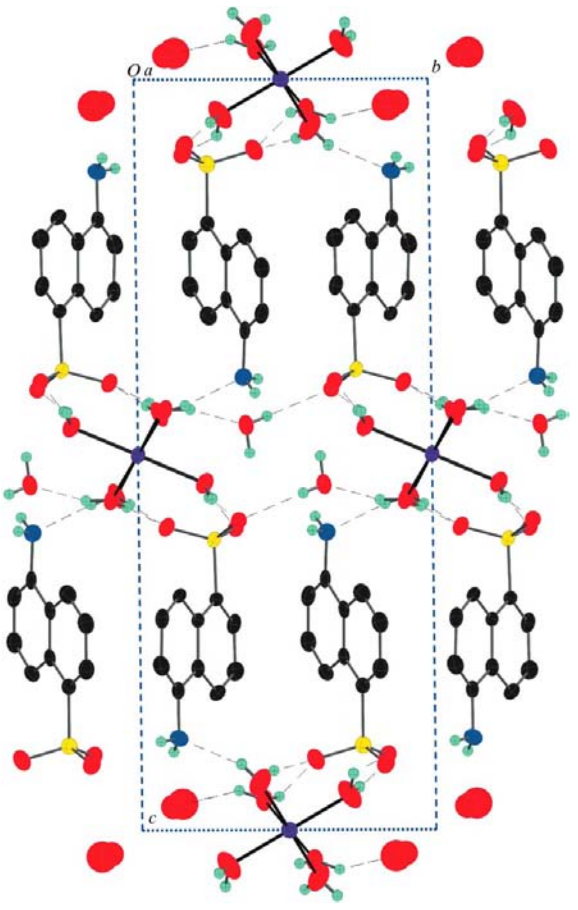


Figure 6
The packing of (IV), viewed down the *a* axis, showing layers of hydrated cations and additional water molecules alternating with layers of anions and connected by O—H···O and N—H···O hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted. Comparison with Fig. 4 shows that the water molecules at (0, 0, *z*) and ($\frac{1}{2}$, $\frac{1}{2}$, *z*) in (II) are missing in (IV).

The Co salt of 5-aminonaphthalene-1-sulfonate, (IV), is not isostructural with the Mn and Ni analogs. It crystallizes as a dihydrate in the triclinic system. The unit cell has almost the same dimensions as the orthorhombic cells of (II) and (III) and the overall structure is quite similar. The asymmetric unit in (IV) (Fig. 5) contains two independent Co^{2+} cations on centers of inversion, six coordinated water molecules, two sulfonate anions and two solvent water molecules (one of which is disordered over two nearby positions). The coordination geometries of the cations are quite regular, with maximum angular deviations of only 1° for Co1 and just under 6° for Co2. The sulfonate groups adopt the same conformation as in (I)–(III), with one O atom eclipsing the naphthalene ring (O—S—C—C torsion angles $< 4^\circ$ in both anions). The anions are packed in a similar herring-bone arrangement with a slightly larger interplanar angle of *ca* 51°. Comparison of the stacking of the anionic and cationic layers in (III) (Fig. 4) with that in (IV) (Fig. 6) shows that they are almost the same. The main difference is that the water molecules at (0, 0, *z*) and ($\frac{1}{2}$, $\frac{1}{2}$, *z*) in (III) are absent in (IV). The anions also appear to have a small extra tilt in (III) that is not present in (IV).

In our previous studies, there is precedence for both differences and a lack of difference in the sulfonate salts of these metals. The Mn, Co and Ni salts of 4-styrenesulfonate are isostructural, with no extra water beyond that coordinated to the metal cations (Leonard *et al.*, 1999). For 4-aminonaphthalene-1-sulfonate, the Co and Ni salts are isostructural orthorhombic trihydrates, while the Mn salt is a monoclinic dihydrate (Morris *et al.*, 2003). And for 5-aminonaphthalene-2-sulfonate, the Mn and Co salts are isostructural monoclinic hexahydrates, while the Ni salt is a triclinic dihydrate with direct Ni—N bonding to the amino group of the sulfonate (Downer *et al.*, 2006). Taken together, these results demonstrate an unexpected structural diversity in these divalent aminonaphthalenesulfonate salts.

Experimental

The starting acid, (I), was crystallized inadvertently from a reaction of itself with $Ni(NO_3)_2·6H_2O$. The Mn salt, (II), was prepared by direct reaction of $Mn(NO_3)_2·6H_2O$ and 5-aminonaphthalene-1-sulfonic acid (1:2 stoichiometry) in aqueous solution. A small amount of NaOH was added to the sulfonic acid to aid in deprotonation prior to introduction of the manganese nitrate. Following approximately 1 h of heating (*ca* 363 K), during which time most of the reactants dissolved, the resulting dark-purple solution was gravity filtered and set out in open air. Upon evaporation of the water, many purple plate-shaped crystals suitable for X-ray diffraction were recovered. The Ni salt, (III), was prepared by combining $NiCO_3$ with 5-aminonaphthalene-1-sulfonic acid (1:2 stoichiometry) in aqueous solution. Following approximately 1 h of heating (*ca* 363 K), during which time the reactants dissolved, the resulting dark-purple solution was gravity filtered and set out in open air. Upon evaporation of the water, many purple clumps of needle-shaped crystals growing from a central point were obtained. The Co salt, (IV), was obtained from a reaction of $Co(OH)_2$ and 5-aminonaphthalene-1-sulfonic acid (1:2 stoichiometry) in water. The reactants dissolved over about 30 min of

Acta Cryst. (2007). C**63**, m604–m609 Genther *et al.* • $C_{10}H_9NO_3S·H_2O$ and $[M(H_2O)_6](C_{10}H_8NO_3S)_2·xH_2O$ (*M* = Mn, Ni and Co) **m607**

heating (*ca* 363 K) and the solution was then gravity filtered. Large (>5 mm) red plate-shaped crystals were left following complete evaporation of the solvent from the dark-red–purple solution.

Compound (I)

Crystal data

$C_{10}H_9NO_3S\cdot H_2O$
$M_r = 241.26$
Monoclinic, $P2_1/c$
$a = 8.1157$ (16) Å
$b = 7.8434$ (16) Å
$c = 16.723$ (3) Å
$\beta = 96.90$ (3)°

$V = 1056.8$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.30$ mm^{-1}
$T = 150$ (2) K
0.30 × 0.06 × 0.03 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
9016 measured reflections

2475 independent reflections
1957 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.120$
$S = 1.04$
2475 reflections

189 parameters
All H-atom parameters refined
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1$^{\rm i}$	0.95 (3)	1.86 (3)	2.803 (3)	172 (2)
N1—H1B···O1$^{\rm ii}$	0.93 (3)	2.01 (3)	2.917 (3)	162 (2)
N1—H1C···O4$^{\rm iii}$	0.93 (3)	1.88 (3)	2.801 (3)	168 (2)
O4—H4A···O3	0.87 (4)	1.89 (4)	2.759 (3)	176 (4)
O4—H4B···O2$^{\rm iv}$	0.89 (5)	2.29 (4)	2.884 (3)	124 (4)

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $x+1, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.

Compound (II)

Crystal data

$[Mn(H_2O)_6](C_{10}H_8NO_3S)_2\cdot 3H_2O$
$M_r = 661.55$
Orthorhombic, $P2_12_12$
$a = 8.3263$ (3) Å
$b = 22.8436$ (7) Å
$c = 7.4940$ (2) Å

$V = 1425.38$ (8) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.68$ mm^{-1}
$T = 140$ (2) K
0.35 × 0.20 × 0.08 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS* and *SAINT-Plus*; Bruker, 2003)
$T_{\rm min} = 0.815$, $T_{\rm max} = 0.947$

47963 measured reflections
6245 independent reflections
6115 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.09$
6245 reflections
250 parameters
All H-atom parameters refined

$\Delta\rho_{\rm max} = 0.55$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Absolute structure: Flack (1983), with 2571 Friedel pairs
Flack parameter: 0.103 (9)

Table 2
Selected bond lengths (Å) for (II).

Mn1—O5	2.1528 (8)	Mn1—O6	2.2137 (8)
Mn1—O4	2.1699 (7)		

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3$^{\rm i}$	0.90 (2)	2.33 (2)	3.1970 (13)	161.2 (18)
N1—H1B···O1$^{\rm ii}$	0.84 (2)	2.41 (2)	3.2251 (12)	161.9 (19)
O4—H4A···O8$^{\rm i}$	0.77 (2)	1.91 (2)	2.6737 (11)	174 (2)
O4—H4B···O2$^{\rm iii}$	0.77 (3)	2.01 (3)	2.7549 (11)	162 (2)
O5—H5A···O8$^{\rm ii}$	0.83 (2)	1.93 (2)	2.7611 (12)	175 (2)
O5—H5B···N1	0.80 (2)	2.14 (2)	2.9279 (13)	167 (2)
O6—H6A···O7$^{\rm iv}$	0.80 (3)	1.99 (3)	2.7698 (11)	168 (3)
O6—H6B···O3$^{\rm iii}$	0.88 (2)	2.04 (2)	2.9054 (11)	169 (2)
O7—H7A···O1	0.77 (2)	2.04 (2)	2.7947 (10)	169 (3)
O8—H8A···O2$^{\rm v}$	0.78 (3)	1.98 (3)	2.7462 (11)	168 (2)
O8—H8B···O1	0.77 (2)	1.99 (2)	2.7421 (11)	165 (2)

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+2$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+2$; (v) $-x+1, -y+1, -z$.

Compound (III)

Crystal data

$[Ni(H_2O)_6](C_{10}H_8NO_3S)_2\cdot 3H_2O$
$M_r = 665.32$
Orthorhombic, $P2_12_12$
$a = 8.1031$ (6) Å
$b = 22.9375$ (18) Å
$c = 7.4607$ (6) Å

$V = 1386.68$ (19) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.93$ mm^{-1}
$T = 140$ (2) K
0.22 × 0.12 × 0.06 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS* and *SAINT-Plus*; Bruker, 2003)
$T_{\rm min} = 0.844$, $T_{\rm max} = 0.950$

14174 measured reflections
3435 independent reflections
3309 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.059$
$S = 1.10$
3435 reflections
250 parameters
11 restraints

All H-atom parameters refined
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Absolute structure: Flack (1983), with 1433 Friedel pairs
Flack parameter: 0.072 (10)

Table 4
Selected bond lengths (Å) for (III).

Ni1—O5	2.0396 (13)	Ni1—O6	2.0844 (13)
Ni1—O4	2.0414 (13)		

Table 5
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3$^{\rm i}$	0.884 (16)	2.356 (17)	3.206 (2)	161 (2)
N1—H1B···O1$^{\rm ii}$	0.858 (17)	2.427 (18)	3.270 (2)	168 (2)
O4—H4A···O8$^{\rm i}$	0.809 (16)	1.872 (17)	2.673 (2)	171 (2)
O4—H4B···O2$^{\rm iii}$	0.826 (17)	1.954 (18)	2.7561 (18)	164 (3)
O5—H5A···O8$^{\rm ii}$	0.824 (17)	1.957 (17)	2.778 (2)	175 (3)
O5—H5B···N1	0.811 (17)	2.155 (18)	2.942 (2)	164 (3)
O6—H6A···O7$^{\rm iv}$	0.794 (17)	1.989 (18)	2.7629 (18)	165 (3)
O6—H6B···O3$^{\rm iii}$	0.823 (17)	2.144 (19)	2.9358 (19)	161 (3)
O7—H7A···O1	0.796 (16)	2.001 (17)	2.7872 (16)	169 (3)
O8—H8A···O2$^{\rm v}$	0.788 (17)	1.971 (18)	2.7435 (18)	166 (3)
O8—H8B···O1	0.793 (16)	1.965 (17)	2.7487 (18)	170 (3)

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

Compound (IV)

Crystal data

$[Co(H_2O)_6](C_{10}H_8NO_3S)_2 \cdot 2H_2O$
$M_r = 647.53$
Triclinic, $P\overline{1}$
$a = 7.013$ (2) Å
$b = 8.710$ (3) Å
$c = 22.385$ (7) Å
$\alpha = 89.394$ (8)°
$\beta = 83.909$ (8)°
$\gamma = 88.271$ (8)°
$V = 1359.1$ (7) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.86$ mm^{-1}
$T = 150$ (2) K
0.41 × 0.18 × 0.02 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*TWINABS*; Sheldrick 2007)
$T_{\min} = 0.702$, $T_{\max} = 0.983$
8586 measured reflections
5584 independent reflections
4971 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.157$
$S = 1.12$
5525 reflections
445 parameters
35 restraints
Only H-atom coordinates refined
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.79$ e Å^{-3}

Table 6
Selected bond lengths (Å) for (IV).

Co1—O9	2.009 (11)	Co2—O12	2.055 (13)
Co1—O7	2.061 (12)	Co2—O11	2.078 (12)
Co1—O8	2.142 (11)	Co2—O10	2.079 (11)

Table 7
Hydrogen-bond geometry (Å, °) for (IV).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···O13^{i}	0.82 (5)	1.95 (8)	2.741 (18)	163 (21)
O8—H8*A*···O5^{ii}	0.82 (5)	1.96 (8)	2.750 (15)	162 (19)
O8—H8*B*···O6^{iii}	0.82 (5)	2.02 (6)	2.832 (15)	172 (17)
O9—H9*A*···N1	0.81 (5)	1.95 (7)	2.748 (19)	166 (23)
O9—H9*B*···O4^{iii}	0.81 (5)	1.95 (6)	2.757 (16)	173 (21)
O10—H10*A*···O2^{iv}	0.82 (5)	2.01 (12)	2.768 (15)	153 (22)
O10—H10*B*···O14^{iv}	0.81 (5)	2.02 (13)	2.73 (2)	144 (21)
O11—H11*A*···O3^{v}	0.81 (5)	1.93 (6)	2.740 (16)	174 (20)
O11—H11*B*···O1	0.82 (5)	2.08 (16)	2.781 (18)	143 (24)
O12—H12*A*···O2	0.82 (5)	1.98 (7)	2.769 (18)	165 (22)
O12—H12*B*···N2^{v}	0.81 (5)	2.04 (10)	2.82 (2)	160 (25)
O13—H13*A*···O5^{vi}	0.82 (5)	2.07 (14)	2.790 (16)	147 (23)
O13—H13*B*···O6	0.83 (5)	2.29 (9)	3.088 (18)	163 (23)

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

For (I), (II) and (III), all H atoms were located in difference Fourier maps and refined isotropically. All crystals of (IV) under investigation were identified as nonmerohedral twins using *RLATT* (Bruker, 2000). Two orientation matrices were assigned to the two different twin components [*GEMINI* (Bruker, 2000) and *SMART* (Bruker, 2003)]. Integration of the data using *SAINT-Plus* (Bruker, 2003) using both orientation matrices deconvoluted the data set into overlapped reflections and reflections originated by only one of the twin components. Correction for absorption, decay and inhomogeneity of the X-ray beam were applied using *TWINABS* (Sheldrick, 2007), where each component was scaled separately, followed by applying the resulting scale factors to the overlapping reflections. The twinning law is a 180° rotation around c^* and the ratio of the two twin components was refined to 0.344 (4):0.656 (4). Equivalent reflections were merged if they originated from the same twin component, or if they originated simultaneously from both components. Thus, a total of 8586 reflections measured were merged to 5584 unique data that include reflections from each of the twin components. All non-H atoms were refined with anisotropic atomic displacement parameters, with the exception of water atom O14, which is disordered over two sites (80:20) and which was refined isotropically; no H atoms were included in the refinement for this water molecule. Other H atoms were located in difference Fourier syntheses and refined with distance restraints of O—H = 0.82 (5) Å, N—H = 0.86 (5) Å and C—H = 0.95 (5) Å, and with $U_{\rm iso}(H) = 1.5U_{\rm eq}(N,O)$ or $1.2U_{\rm eq}(C)$.

For all compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

Funding from the Office of Naval Research (grant No. N00014-97-1-0409) to purchase the CCD detector at the University of Toledo is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3173). Services for accessing these data are described at the back of the journal.

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