Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Two novel mixed-ligand complexes containing organosulfonate ligands

Mingtian Li,* Jun Huang, Xuan Zhou, Hua Fang and Liyun Ding

Key Laboratory of Fiber Optic Sensing Technology and Information Processing (Ministry of Education), Wuhan University of Technology, Wuhan, Hubei 430070, People's Republic of China
Correspondence e-mail: limt63646616@yahoo.com.cn

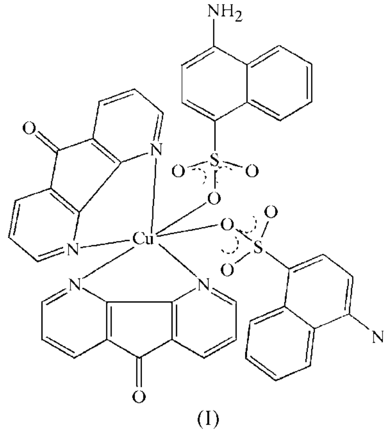
Received 25 April 2008
Accepted 27 May 2008
Online 21 June 2008

The structures reported herein, *viz.* bis(4-aminonaphthalene-1-sulfonato-κO)bis(4,5-diazafluoren-9-one-κ^2N,N')copper(II), $[Cu(C_{10}H_8NO_3S)_2(C_{11}H_6N_2O)_2]$, (I), and poly[[[diaquacadmium(II)]-bis(μ-4-aminonaphthalene-1-sulfonato)-κ^2O:N;κ^2N:O] dihydrate], $\{[Cd(C_{10}H_8NO_3S)_2(H_2O)_2]\cdot 2H_2O\}_n$, (II), are rare examples of sulfonate-containing complexes where the anion does not fulfill a passive charge-balancing role, but takes an active part in coordination as a monodentate and/or bridging ligand. Monomeric complex (I) possesses a crystallographic inversion center at the Cu^{II} atom, and the asymmetric unit contains one-half of a Cu atom, one complete 4-aminonaphthalene-1-sulfonate (ans) ligand and one 4,5-diazafluoren-9-one (DAFO) ligand. The Cu^{II} atom has an elongated distorted octahedral coordination geometry formed by two O atoms from two monodentate ans ligands and by four N atoms from two DAFO molecules. Complex (II) is polymeric and its crystal structure is built up by one-dimensional chains and solvent water molecules. Here also the cation (a Cd^{II} atom) lies on a crystallographic inversion center and adopts a slightly distorted octahedral geometry. Each ans anion serves as a bridging ligand linking two Cd^{II} atoms into one-dimensional infinite chains along the [010] direction, with each Cd^{II} center coordinated by four ans ligands *via* O and N atoms and by two aqua ligands. In both structures, there are significant π–π stacking interactions between adjacent ligands and hydrogen bonds contribute to the formation of two- and three-dimensional networks.

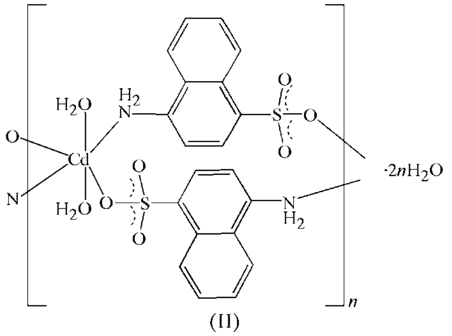
Comment

Owing to their weak coordination abilities with regard to transition metal atoms, most of the reported complexes containing organosulfonate ligands are aqua–metal salts, and the sulfonate species only acts as a counter-anion to balance the charge within the complex (Kosnic *et al.*, 1992; Shubnell *et al.*, 1994; Gunderman *et al.*, 1997). In some rare cases, however, the sulfonate ligand can also bind to the metal centers in the presence of ancillary ligands (Cai, Chen, Liao, Feng & Chen, 2001; Cai, Chen, Liao, Yao *et al.*, 2001; Chen *et al.*, 2002). It is well known that the coordination behavior of one ligand can be influenced by the others within a mixed-ligand complex.

In this respect, 4-aminonaphthalene-1-sulfonate could be a potential bridging ligand, since it contains sulfonate and NH_2 groups located at opposite sides of a benzene ring, and could exhibit versatile coordination modes in the presence of adequate ancillary ligands. This behavior would be similar to that of 4-aminobenzenesulfonate (Endres, 1984; Brodersen & Beck, 1987; Starynowicz, 1992; Shakri & Haussuhl, 1992*a*,*b*; Gunderman *et al.*, 1996; Zhou *et al.*, 2004). For 4-aminobenzenesulfonate, it is common that the two functional groups simultaneously bind to metal ions; however, to our knowledge, no example of such behavior has been reported for 4-aminonaphthalene-1-sulfonate (ans). As part of an investigation of the coordination behavior of sulfonates, a series of mixed-ligand complexes have been synthesized so far; in our previous work, the sulfonate group behaved only as a charge-balancing counter-anion (Li *et al.*, 2005*a*,*b*, 2006, 2007). In order to obtain complexes in which the sulfonate group binds directly to the metal, ligands with a large conjugate plane, examples being 2,2′-bipyridine, 1,10-phenanthroline and dipyridophenazine, were used as ancillary ligands. We present here two novel complexes in which the sulfonate group exhibits such behavior, *viz.* $[Cu(ans)_2(DAFO)_2]$, (I), and $\{[Cd(ans)_2(H_2O)_2]\cdot 2H_2O\}_n$, (II) (where DAFO is 4,5-diazafluoren-9-one).



(I)



(II)

The asymmetric unit of (I) consists of half a Cu atom, one complete ans ion and one neutral DAFO ligand (Fig. 1 and

DOI: 10.1107/S0108270108016041

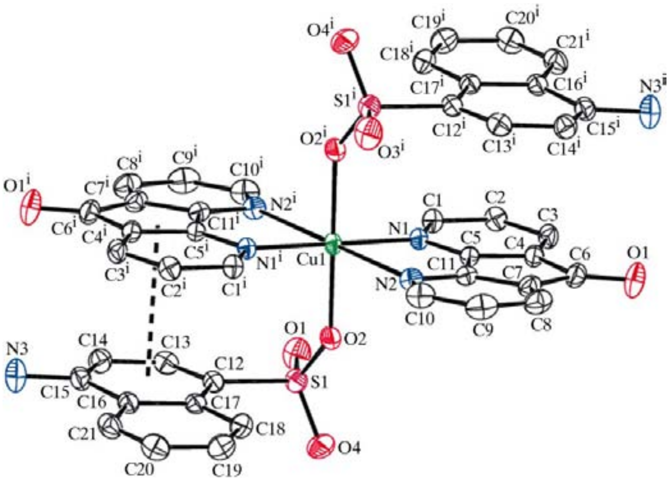


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. [Symmetry code: (i) $-x + 2, -y + 1, -z$.]

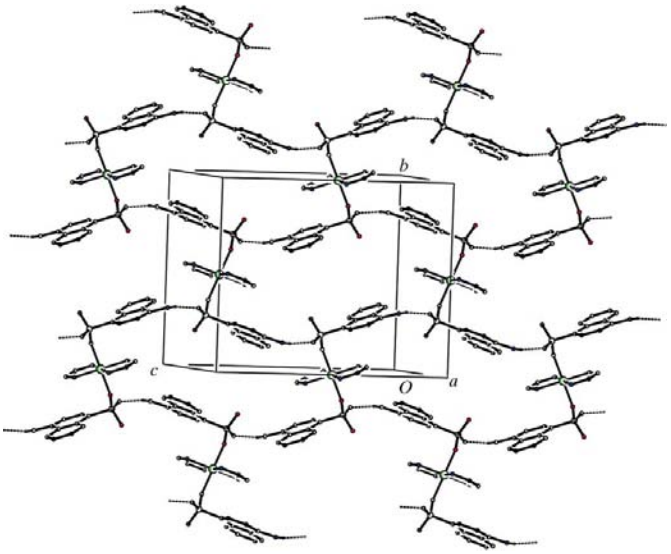


Figure 2
Hydrogen-bonded two-dimensional sheets in (I). Some atoms have been omitted for clarity and hydrogen bonds are shown as dashed lines.

Table 1). The $\mathrm{Cu^{II}}$ atom lies on a crystallographic inversion center and has an elongated distorted octahedral coordination geometry formed by two O atoms from two monodentate ans ligands and by four N atoms from two DAFO molecules; the manner of coordination is unusual in that the elongated Jahn–Teller (J–T) axis of the molecule lies along one of the N—Cu—N vectors [Cu1—N2 = 2.6231 (18) Å] and not on the O—Cu—O axis [Cu1—O2 = 1.989 (14) Å and O2—Cu1—O2$^{\mathrm{i}}$ = 180°], which is occupied by ans counter-ions. As far as we know, this is one of the few examples of $\mathrm{N_2O_2N_2'}$ coordination to a $\mathrm{Cu^{II}}$ center with two anions bound *trans* in the equatorial plane and N atoms of the chelate directed along the J–T axis (Menon & Rajasekharan, 1998). This $\mathrm{N_2}X_2\mathrm{N_2'}$ geometry has been observed in other $\mathrm{Cu^{II}}$ complexes with the 4,5-diazafluorene template and simple anions such as $\mathrm{Cl^-}$ or $\mathrm{Br^-}$ (Menon & Rajasekharan, 1998), while complexes with transition metals other than $\mathrm{Cu^{II}}$, such as $\mathrm{Re^{I}}$ (Yam *et al.*, 1998) and $\mathrm{Ni^{II}}$ (Xiong *et al.*, 1996), typically exhibit a more symmetrical coordination.

Both ligands are planar within an r.m.s. deviation of 0.002 Å, with largest departures from the least-squares plane of 0.055 (2) Å for atom C9 in DAFO and 0.038 (2) Å for atom C13 in ans. Owing to the characteristic conjugated structures of both ligands, there are not only intramolecular but also intermolecular π–π stacking interactions between adjacent planes. To describe the latter let us define *Cg*1 as the centroid of the C12–C17 benzene ring in ans and $Cg2^{\mathrm{iii}}$ as the centroid of the C4–C7/C11 ring in a symmetry-related DAFO molecule [symmetry code: (iii) $x + 2, -y + 1, -z$], with α the dihedral angle between the two rings, and β the angle between the intercentroid vector and the *Cg*1 plane. The values $Cg1\cdots Cg2^{\mathrm{iii}}$ = 3.3570 (12) Å, α = 4.44° and β = 19.52° indicate that there is a significant intramolecular π–π aromatic stacking interaction (Evans & Boeyens, 1989). At the same time, there is a significant intermolecular π–π stacking interaction involving *Cg*1 and a neighboring pyridine ring [$Cg1\cdots Cg3^{\mathrm{iv}}$ = 3.5232 (11) Å; *Cg*3 is the centroid of the C7–C11/N2 ring; symmetry code: (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$].

Hydrogen-bond interactions play a key role in the formation of two-dimensional sheets and three-dimensional

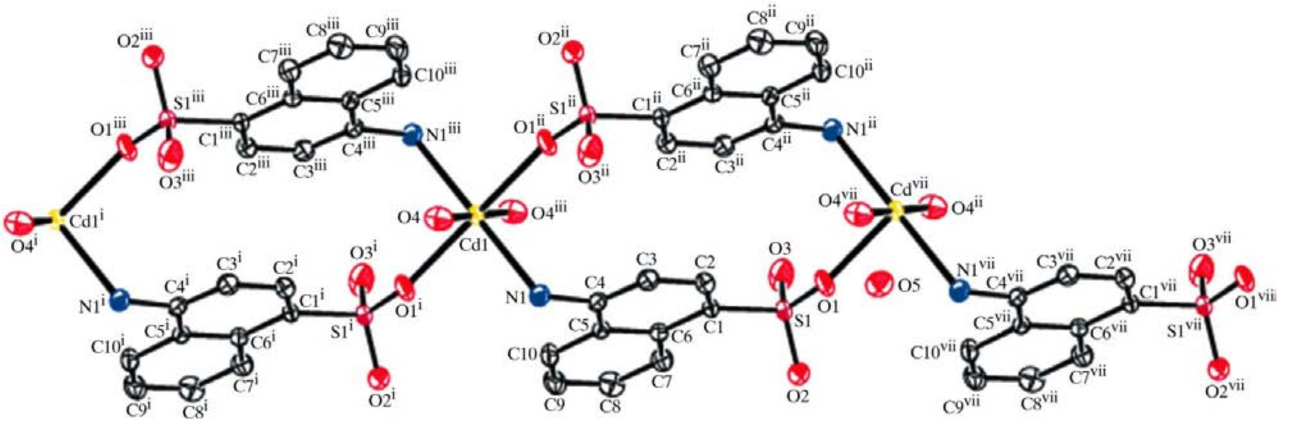


Figure 3
The molecular structure of (II), showing displacement ellipsoids at the 30% probability level. [Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 2, -z + 2$; (iii) $-x + 2, -y + 2, -z + 2$; (vii) $x - 1, y, z$.]

networks and in the stabilization of the crystal structure of (I). As shown in Fig. 2, one neutral complex links four neighboring complex molecules *via* N—H···O(S) hydrogen bonds (Table 2), forming two-dimensional layers extending in the (100) plane. Nonclassical C—H···O and C—H···N hydrogen bonds, as well as the previously discussed π–π stacking interactions, take part in the formation of a three-dimensional network.

Complex (II) (Fig. 3) also possesses a crystallographic inversion center, this time located at the Cd^{II} atom, which displays a distorted octahedral geometry. The Cd atom is coordinated by four O atoms from two ans ligands and two water molecules, and by two N atoms belonging to another two ans anions, a situation similar to that in complexes of 4-aminobenzenesulfonate (abs) with Zn^{II}, Co^{II} and Cd^{II} (Shakeri & Haussuhl, 1992*a*,*b*; Zhou *et al.*, 2004). The Cd—O$_{water}$ distances (Table 3) are in agreement with that in $[Cd(\mu_2\text{-abs})_2(H_2O)_2]_n$ [2.303 (2) Å; Zhou *et al.*, 2004], and the Cd—O(S) distance is slightly longer than its counterpart in $[Cd(\mu_2\text{-abs})_2(H_2O)_2]_n$ [2.294 (2) Å]. The Cd—N distance is close to that in $[Cd(\mu_2\text{-abs})_2(H_2O)_2]_n$ [2.373 (3) Å] and longer than the equivalent Cd—N distances in $[Cd(en)_2(H_2O)_2](ans)_2\cdot 2H_2O$ [en is ethylenediamine; 2.240 (2) and 2.280 (2) Å; Li *et al.*, 2006].

Each ans ligand in (II) links two cadmium(II) cations though O and N atoms; there are two such centrosymmetric bridges per Cd pair, defining a dimeric unit with a Cd···Cd distance of 9.2553 (6) Å (Fig. 3). Concatenation of these dimers leads to a doubly bridged one-dimensional polymeric chain extending along [010]. The centroid–centroid distance, *Cg*1···*Cg*2^{v}, between the aromatic rings in two symmetry-related ans ligands is 3.5676 (9) Å [*Cg*1 and *Cg*2 are the centroids of the C1–C6 and C5–C10 rings, respectively; symmetry code: (v) $-x + 1, -y + 2, -z + 1$], while α and β are 1.93 and 17.48°, respectively, indicating a significant π–π stacking interaction.

Hydrogen bonding plays a key role in the formation of a three-dimensional network through the linkage of chains and solvent water molecules. Fig. 4 shows the way in which this is achieved, with neighboring chains (pointing out of the projection plane in the [100] direction) linked through an extensive hydrogen-bond network involving all of the water molecules in a series of O—H···O(water), O—H···O(S) and N—H···O(S) interactions (Table 4).

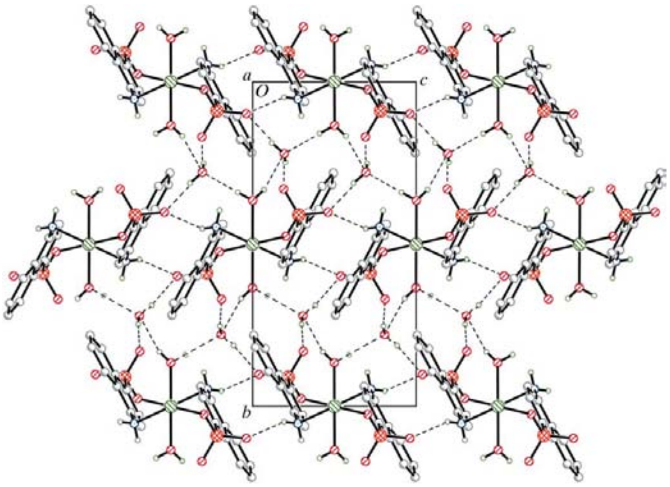


Figure 4
The molecular packing of (II), with hydrogen bonds shown as dashed lines. Some atoms have been omitted for clarity.

Experimental

For the preparation of complex (I), an acetonitrile solution (10 ml) of 4,5-diazafluoren-9-one (0.183 g, 1 mmol) was added to an aqueous solution (20 ml) of $Cu(OAc)_2\cdot H_2O$ (0.100 g, 0.5 mmol) under constant stirring. After the mixture had been stirred for 2 h at 298 K, the solution was treated with sodium 4-aminonaphthalene-1-sulfonate tetrahydrate (0.32 g, 1 mmol) in methanol (10 ml). After filtration, the red solution was allowed to stand at room temperature. Well shaped red block-like crystals were obtained by slow evaporation of the solvent over a period of about a week. Complex (II) was obtained as a by-product of the reaction of dipyridophenazine (0.283 g, 1 mmol), $Cd(OAc)_2\cdot 2H_2O$ (0.133 g, 0.5 mmol) and sodium 4-aminonaphthalene-1-sulfonate tetrahydrate (0.32 g, 1 mmol) in a mixed solvent of water and acetonitrile (2:1 *v*/*v*, 30 ml).

Compound (I)

Crystal data

$[Cu(C_{10}H_8NO_3S)_2(C_{11}H_6N_2O)_2]$
$M_r = 872.36$
Orthorhombic, *Pbca*
$a = 14.8903\ (13)$ Å
$b = 13.9907\ (12)$ Å
$c = 17.1961\ (15)$ Å
$V = 3582.4\ (5)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.80$ mm^{-1}
$T = 273\ (2)$ K
0.48 × 0.14 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.701$, $T_{max} = 0.925$
22653 measured reflections
4319 independent reflections
3396 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.098$
$S = 1.02$
4319 reflections
276 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

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

Cu1—N1	1.9872 (14)	S1—O4	1.4413 (16)
Cu1—O2	1.9890 (14)	S1—O3	1.4442 (17)
Cu1—N2	2.6231 (18)	S1—C12	1.7674 (19)
Cu1—N2^{i}	2.6231 (18)	C15—N3	1.379 (3)
O2—S1	1.4853 (15)		
N1^{i}—Cu1—O2	92.89 (6)	N2^{i}—Cu1—O2	93.80 (8)
N1—Cu1—O2	87.11 (6)		

Symmetry code: (i) $-x + 2, -y + 1, -z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*B*···O3^{ii}	0.87 (4)	2.28 (4)	3.142 (3)	168 (3)

Symmetry code: (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Compound (II)

Crystal data

$[Cd(C_{10}H_8NO_3S)_2(H_2O)_2]\cdot 2H_2O$
$M_r = 628.93$
Monoclinic, $P2_1/c$
$a = 9.2553$ (6) Å
$b = 15.6133$ (9) Å
$c = 8.1857$ (5) Å
$\beta = 106.305$ (1)°
$V = 1135.31$ (12) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.21$ mm^{-1}
$T = 273$ (2) K
0.40 × 0.37 × 0.32 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.62$, $T_{\max} = 0.68$
7462 measured reflections
2729 independent reflections
2613 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.052$
$S = 1.07$
2729 reflections
185 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}

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

Cd1—O1^{i}	2.2620 (13)	N1—C4	1.428 (2)
Cd1—O4	2.3060 (13)	S1—O3	1.4465 (14)
Cd1—N1	2.3549 (14)	S1—O2	1.4490 (13)
O1—S1	1.4597 (14)		
O1^{i}—Cd1—O4	82.48 (6)	O1^{ii}—Cd1—N1	94.46 (6)
O1^{ii}—Cd1—O4	97.52 (6)	O4—Cd1—N1	85.27 (5)
O1^{i}—Cd1—N1	85.54 (6)	O4^{iii}—Cd1—N1	94.73 (5)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O5^{iv}	0.82 (3)	1.96 (3)	2.778 (2)	171 (3)
O4—H4B···O5^{ii}	0.75 (3)	2.23 (3)	2.943 (2)	159 (3)
N1—H1A···O2^{v}	0.77 (3)	2.31 (3)	3.016 (2)	154 (2)
O5—H5A···O2^{vi}	0.81 (3)	1.94 (3)	2.7394 (19)	171 (3)
O5—H5B···O3	0.81 (3)	1.94 (3)	2.738 (2)	167 (3)

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

H atoms of water molecules and amine groups were located in difference Fourier maps and were refined subject to an O—H DFIX restraint (Sheldrick, 2008) of 0.82 (3) Å and an N—H DFIX restraint of 0.86 (3) Å. C-bound H atoms were placed in geometrically idealized positions and treated as riding [C—H = 0.93 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C)].

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXS97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Key Project of the National Science Foundation of China (grant No. 60537050).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3074). Services for accessing these data are described at the back of the journal.

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