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# 3,5-Dimethylpyrazole promoted sulfonation of acetic anhydride by H<sub>2</sub>SO<sub>4</sub> to sulfoacetic acid and methanedisulfonic acid, and crystal structures of the complexes with Co<sup>2+</sup>, Zn<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup> and Cs<sup>+</sup>

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# ABSTRACT

Sulfuric acid can sulfonate acetic anhydride (but not acetic acid) to sulfoacetic acid, and also to methanedisulfonic acid in the presence of 3,5-dimethylpyrazole. Under the experimental conditions employed, sulfonation of 3,5-dimethylpyrazole with concentrated sulfuric acid in acetic anhydride/acetic acid as solvent leads to a mixture of approximately 47 mol% 3,5-dimethylpyrazole-4-sulfonic acid, 34 mol% sulfoacetic acid and 19 mol% methanedisulfonic acid, as determined by <sup>1</sup>H NMR spectroscopy. The Co<sup>2+</sup>,  $Zn^{2+}$ ,  $Ba^{2+}$  and  $Pb^{2+}$  complexes of the sulfoacetate ligand, as well as the Cs<sup>+</sup> complex of the methanedisulfonate ligand were isolated upon crystallization of the compounds obtained from the reaction of the above ligand mixture with the corresponding metal oxide or carbonate in water. Single-crystal X-ray crystallography of Co(O<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub>, Zn(O<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub>, Ba(O<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>)(H<sub>2</sub>O), Pb(O<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>)(H<sub>2</sub>O) and Cs<sub>2</sub>(O<sub>3</sub>SCH<sub>2</sub>SO<sub>3</sub>) reveals a variety of new coordination modes of the two sulfonated ligands within those structures.

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Inorganica Chimica Acta

# 1. Introduction

During our recent studies of copper corrosion inhibitors [1,2], we became interested in the synthesis of 3,5-dimethylpyrazole-4-sulfonic acid. To avoid the rather cumbersome traditional procedure using the barium sulfonate intermediate [3] (which we have previously employed for the preparation of pyrazole-4-sulfonic acid) [4,5], we decided to use an alternative published method for the sulfonation of pyrazoles. According to this paper, the preparation consisted of the reaction of 3,5-dimethylpyrazole with concentrated sulfuric acid in an acetic anhydride/acetic acid solvent mixture, and the solid product was isolated from the cooled reaction mixture by filtration and washing with dry benzene [6]. In our hands, however, crystallization of its metal complexes unexpectedly turned out sulfoacetates, and even more surprisingly, methane-disulfonates instead of 3,5-dimethylpyrazole-4-sulfonates. An examination of the literature revealed that sulfuric acid is indeed able to sulfonate an acetic anhydride/acetic acid mixture to sulfoacetic acid via an acetylsulfuric acid intermediate [7]. Sulfoacetic acid and methane-disulfonic acid have also been observed as by-products in the preparation of acetic acid by the Pt-catalyzed oxidative carbonylation of methane in concentrated sulfuric acid

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[8]. Very few metal complexes of these two ligands have been structurally characterized. With sulfoacetate, the X-ray crystal structures of the disilver(I)- [9] and the monosodium-salts [10] are known, as well as of three platinum(II)-amine complexes [11]. With methanedisulfonate, the structures of the disodium-[12], dipotassium- [13], calcium [14], cadmium- [14a,c], disilver(I)-[15], ytterbium- [16] and samarium-salts [17] have been reported, as well as the ones with additional 1,10-phenanthroline- or other chelating aromatic diamine ligands with cobalt(II) [18], nickel(II) [19], copper(II) [20], and cadmium [21] and of the free ligand as the dihydrate [22]. Herein we report the <sup>1</sup>H NMR analysis of the sulfonated 3,5-dimethylpyrazole/acetic anhydride/acetic acid mixture, as well as the preparation and single crystal X-ray crystallographic characterization of the Co<sup>2+</sup>, Zn<sup>2+</sup>, Ba<sup>2+</sup> and Pb<sup>2+</sup> complexes of the resulting sulfoacetate-, and the Cs<sup>+</sup> complex of the methanedisulfonate ligand.

# 2. Experimental

# 2.1. General

All commercially available reagents were used as received. NMR spectra were recorded on a 400 MHz Jeol JNM-ECP400 spectrometer at room temperature in CDCl<sub>3</sub>. X-ray diffraction data were collected at 100 K (except for the cobalt complex, 296 K) from a



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single crystal mounted atop a glass fiber with a Bruker SMART APEX II diffractometer using graphite-monochromated Mo K $\alpha$ ( $\lambda$  = 0.71073 Å) radiation. The structures were solved employing the SHELXTL-direct methods program and refined by full-matrix least-squares on  $F^2$ , using the APEX2 v2008.2-0 software package [23]. Crystallographic details are summarized in Table 1.

# 2.2. Synthesis

Sulfoacetic acid and methanedisulfonic acid were obtained in mixture with 3,5-dimethylpyrazole-4-sulfonic acid during the sulfonation of 3,5-dimethylpyrazole with  $H_2SO_4$  in acetic anhydride/ acetic acid [6], and were used without further purification (Scheme 1).  $H_2SO_4$  (95–98%, 5.3 ml, 9.8 g, 0.10 mol) was slowly added to 14.2 ml (15.3 g, 0.15 mol) acetic anhydride under stirring. After cooling to room temperature, a solution of 9.61 g (0.10 mol) 3,5-dimethylpyrazole in 5.0 ml (5.2 g, 0.087 mol) glacial acetic acid was added dropwise. After stirring for 3 days at room temperature (protected from moisture), the mixture was refluxed for 30 min and then kept in a refrigerator for one day. The resulting solid was filtered, washed with benzene and dried in vacuum. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.00 (s, 2H, sulfoacetic acid); 3.49 (s, 2H, methanedisulfonic acid); 2.41 (s, 6H, 3,5-dimethylpyrazole-4-sulfonic acid).

Metal complexes were prepared by dissolving the ligand mixture and the corresponding metal compound ( $CoCO_3$ , ZnO, BaCO\_3, PbO and  $Cs_2CO_3$ ) in water. A few single crystals suitable for X-ray diffraction were grown from those solutions after acetone vapor diffusion (Zn, Ba and Pb – colorless, Co – red, Cs – yellow). In each case, crystals with only one type of ligand were obtained, while the other possible complexes were left dissolved in the mother liquor.

# 3. Results and discussion

### 3.1. NMR characterization

<sup>1</sup>H NMR of the crystalline reaction product in CDCl<sub>3</sub> revealed the presence of three compounds (see reaction equation above). The signal at 2.41 ppm was assigned to 3,5-dimethylpyrazole-4sulfonic acid (reported value in DMSO-d<sub>6</sub> is 2.28 ppm),<sup>6</sup> while the signals at 3.49 ppm and 4.00 ppm were attributed to methanedisulfonic acid and sulfoacetic acid, respectively (a sample of wet sulfoacetic acid from Aldrich has a chemical shift of 4.04 ppm in CDCl<sub>3</sub>). The integration ratio of 7.33:1:1.73 of those three signals

Table	1			
C		~ 6	~~~	

Summary of crystallographic data.

corresponds to an approximate composition of 47 mol% 3,5-dimethylpyrazole-4-sulfonic acid, 19 mol% methanedisulfonic acid and 34 mol% sulfoacetic acid. Recrystallization from water did not change the ratio between the products significantly. Skipping the reflux during the synthesis still led to sulfoacetic acid but only traces of methanedisulfonic acid, and some unreacted 3,5-dimethylpyrazole was detected in the <sup>1</sup>H NMR spectrum. We have also performed the same reaction under the original conditions without 3,5-dimethyl-pyrazole, and found sulfoacetic acid but no methanedisulfonic acid in the resulting reaction mixture by <sup>1</sup>H NMR. The reaction of H<sub>2</sub>SO<sub>4</sub> and acetic anhydride only (no acetic acid) produced similar results, while in the case of H<sub>2</sub>SO<sub>4</sub> and acetic acid only (no acetic anhydride), no sulfonation was observed at all. These results show that only the more reactive acetic anhydride undergoes sulfonation to sulfoacetic acid, even in the absence of 3.5-dimethyl-pyrazole (via protonation by sulfuric acid producing acetic acid and acetylsulfuric acid, with the latter undergoing a subsequent rearrangement to sulfoacetic acid [7]). Further sulfonation to methanedisulfonic acid occurs in the presence of 3,5-dimethylpyrazole.

# 3.2. Description of the crystal structures

# 3.2.1. Co(O<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub> [Co(SA)(H<sub>2</sub>O)<sub>3</sub>]

Since the crystals of the cobalt complex turned opaque at 100 K and did not diffract at that temperature, data collection was carried out at room temperature (296 K). The Co<sup>2+</sup> ion is 6-coordinate, in an approximately octahedral environment, by three O-atoms from two different sulfoacetate ligands (two from acetate groups and one from a sulfonate group), and three H<sub>2</sub>O molecules (Fig. 1, Table 2). The coordination mode of the SA ligand, which is both chelating and bridging, can be described as  $\mu$ -sulfonato-1 $\kappa$ O-acetato-1 $\kappa$ O:2 $\kappa$ O'. The resulting coordination polymer consists of planar snake-like undulating chains with perpendicularly bound water molecules on each side, and in-plane water molecules forming intra-chain hydrogen bonds (Fig. 2). The overall 3D structure is the result of a web of inter-chain hydrogen bonds (Table 3) connecting the polymeric chains.

# 3.2.2. Zn(O<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub> [Zn(SA)(H<sub>2</sub>O)<sub>3</sub>]

The zinc sulfoacetate complex is isostructural with the corresponding cobalt complex (see above), with nearly identical structural parameters.

5 5 8 I					
	$Co(SA)(H_2O)_3$	$Zn(SA)(H_2O)_3$	Ba(SA)(H <sub>2</sub> O)	$Pb(SA)(H_2O)$	Cs <sub>2</sub> (MDS)
Formula	C <sub>2</sub> H <sub>8</sub> CoO <sub>8</sub> S	C <sub>2</sub> H <sub>8</sub> O <sub>8</sub> SZn	C <sub>2</sub> H <sub>3</sub> BaO <sub>5.5</sub> S	C <sub>2</sub> H <sub>4</sub> O <sub>6</sub> PbS	CH <sub>2</sub> Cs <sub>2</sub> O <sub>6</sub> S <sub>2</sub>
Formula weight	251.07	257.51	284.44	363.30	439.97
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	C2/m (No. 12)	C2/c (No. 15)
a (Å)	6.3701(2)	6.4992(1)	5.2849(1)	10.3837(2)	13.3316(2)
b (Å)	9.0071(2)	8.8577(1)	8.2004(2)	7.1228(1)	8.0022(1)
c (Å)	13.5190(4)	13.4436(2)	13.6441(4)	9.5745(2)	7.8672(1)
α (°)	90	90	90	90	90
β (°)	90.757(1)	90.000(1)	95.614(2)	120.680(1)	91.624(1)
γ (°)	90	90	90	90	90
$V(Å^3)$	775.60(4)	773.92(2)	588.48(3)	609.02(2)	838.95(2)
Z	4	4	4	4	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	2.150	2.210	3.211	3.962	3.483
$\mu ({\rm mm}^{-1})$	2.491	3.453	7.059	28.014	9.169
Reflections collected/unique	26,815/2420	10,476/1335	7697/1648	7145/1559	16,563/1767
Observed reflections	2090	1227	1195	1504	1570
Goodness-of-fit (on $F^2$ )	1.051	1.077	1.052	1.102	1.043
$R(F); R_w(F) (I > 2\sigma(I))$	0.0229; 0.0578	0.0184; 0.0431	0.0440; 0.0925	0.0170; 0.0364	0.0179; 0.0355



Scheme 1. Products identified in the sulfonation reaction mixture.



**Fig. 1.** Crystal structure of  $Co(SA)(H_2O)_3$ , showing the coordination sphere around Co, as well as the coordination mode of the SA ligand. Symmetry codes: (a) -x + 1, y - 0.5, -z + 0.5; (b) -x + 1, y + 0.5, -z + 0.5.

### Table 2

Selected bond lengths (Å) for Co(SA)(H2O)3.

Co1-O1: 2.073(1)	Co1-07: 2.093(1)	S1-03: 1.469(1)
Co1-O2b: 2.086(1)	Co1-O8: 2.061(1)	S1-04: 1.447(1)
Co1-O3: 2.131(1)	C1-O1: 1.254(2)	S1-05: 1.449(1)
Co1-O6: 2.072(1)	C1-O2: 1.246(2)	

Symmetry transformations used to generate equivalent atoms: (b) -x + 1, y + 0.5, -z + 0.5.

# 3.2.3. Ba(O<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>)(H<sub>2</sub>O) [Ba(SA)(H<sub>2</sub>O)]

The Ba<sup>2+</sup> ion is 10-coordinate, by nine O-atoms from six different sulfoacetate ligands (four from acetate groups and five from sulfonate groups), and an H<sub>2</sub>O molecule (Fig. 3, Table 4). The coordination polyhedron around Ba<sup>2+</sup> is in between a bicapped square antiprism and a decatetrahedron, the two most common coordination polyhedra for coordination number ten [24]. The coordination mode of the SA ligand is  $\mu_6$ -sulfonato-1 $\kappa^2$ O, O';2 $\kappa$ O';4 $\kappa$ O''-acetato-1:5 $\kappa$ O;5:6 $\kappa$ O'. The H<sub>2</sub>O molecule, which is disordered over two positions, is H-bonded to carboxylate groups of the SA ligands (O6...O2: 2.72–2.99 Å). An excerpt from the packing diagram of Ba(SA)(H<sub>2</sub>O) is shown in Fig. 4.

# 3.2.4. Pb(O<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>)(H<sub>2</sub>O) [Pb(SA)(H<sub>2</sub>O)]

The Pb<sup>2+</sup> ion is 9-coordinate, by seven O-atoms from five different sulfoacetate ligands (four from acetate groups and three from sulfonate groups), and two H<sub>2</sub>O molecules (Fig. 5, Table 5). The coordination polyhedron around Pb<sup>2+</sup> is a slightly distorted monocapped square antiprism [24]. The coordination mode of the SA ligand is  $\mu_5$ -sulfonato-1 $\kappa^2$ O,O';2 $\kappa$ O''-acetato-3:4 $\kappa$ O;4:5 $\kappa$ O'. The H<sub>2</sub>O molecule, which lies on a crystallographic mirror plane, is H-bonded to sulfonate groups of the SA ligands (O4...O3: 2.779 Å; O4–H4: 0.87 Å; H4...O3: 1.93 Å; O4–H4...O3: 166°). An excerpt from the packing diagram of Pb(SA)(H<sub>2</sub>O) is shown in Fig. 6.

# 3.2.5. Cs<sub>2</sub>(O<sub>3</sub>SCH<sub>2</sub>SO<sub>3</sub>) [Cs<sub>2</sub>(MDS)]

The Cs<sup>+</sup> ion is 9-coordinate, by O-atoms from six different methanedisulfonate ligands (Fig. 7, Table 6). The coordination polyhedron around Cs<sup>+</sup> is in between a tricapped trigonal prism and a monocapped square antiprism, the two most common coordination polyhedra for coordination number nine [24]. The coordination mode of the MDS ligand is  $\mu_{12}$ -methanedisulfonato-1:2:3 $\kappa^3 O^1$ ;3:4:5 $\kappa^3 O^1$ ;5:6:7 $\kappa^3 O^{1''}$ ;6:8:9 $\kappa^3 O^2$ ;4:8:10 $\kappa^3 O^2$ ;9:11:12  $\kappa^3 O^{2''}$  (Fig. 8). An excerpt from the packing diagram of Cs<sub>2</sub> (MDS) is shown in Fig. 9.



Fig. 2. View of the packing in Co(SA)(H<sub>2</sub>O)<sub>3</sub> along the *a* axis, showing the content of the unit cell and the undulating coordination polymer chains within the crystal.

S. Jianrattanasawat, G. Mezei/Inorganica Chimica Acta 384 (2012) 318-323

D-H…A	D–H (Å)	H…A (Å)	D…A (Å)	D-H…A (°)	Symmetry operator for A
O6 H6b O1	0.76	2.11	2.730	139	-x + 1, $y + 0.5$ , $-z + 0.5$
O6 H6b O2	0.76	2.45	3.098	144	x, y + 1, z
O6 H6a O5	0.81	2.00	2.772	161	-x, -y + 2, -z
07 H7a 04	0.77	2.16	2.866	153	-x, y + 0.5, -y + 0.5
O7 H7b O5	0.78	2.10	2.867	168	x, -y + 1.5, z + 0.5
O8 H8a O3	0.77	2.08	2.832	165	-x + 1, -y + 2, -z
08 H8b 04	0.73	2.13	2.845	168	x + 1, y, z

 Table 3

 Summary of hydrogen bonding data for Co(SA)(H<sub>2</sub>O)<sub>3</sub>.



**Fig. 3.** Crystal structure of Ba(SA)(H<sub>2</sub>O), showing the coordination sphere around Ba, as well as the coordination mode of the SA ligand. The hydrogen atoms of the disordered, bridging water molecule (O6, only one position shown) could not be located from the difference Fourier map. Symmetry codes: (a) -x + 0.5, y - 0.5, -z + 1.5; (b) -x + 1, -y + 1, -z + 2; (c) -x + 1.5, y - 0.5, -z + 1.5; (d) x, y - 1, z; (e) x - 1, y - 1, z.

## Table 4

Selected bond lengths (Å) for Ba(SA)(H<sub>2</sub>O).

Ba1-01: 2.929(5)	Ba1-O3c: 2.791 (5)	C1-O1: 1.243(9)
Ba1-01a: 2.719(5)	Ba1-O4a: 2.953(5)	C1-O2: 1.238(8)
Ba1-02: 2.966(6)	Ba1-O4d: 2.722(5)	S1-03: 1.460(5)
Ba1-O2b: 2.817(6)	Ba1-05e: 2.814(5)	S1-04: 1.460(5)
Ba1-03a: 2.964(5)	Ba1-O6: 2.80(5)	S1-05: 1.440(5)

Symmetry transformations used to generate equivalent atoms: (a) -x + 0.5, y - 0.5, -z + 1.5; (b) -x + 1, -y + 1, -z + 2; (c) -x + 1.5, y - 0.5, -z + 1.5; (d) x, y - 1, z; (e) x - 1, y - 1, z.

Table	5		

Selected bond lengths (Å) for $Pb(SA)(H_2O)$ .			
Pb1a-O1c: 2.531(2)	Pb1a-O3: 2.771(3)	C1-01: 1.259(2)	
Pb1a-O1d: 2.704(2)	Pb1a-O3b: 2.771(3)	C1-O1b: 1.259(2	
D = 1 + 01 + 2704(2)	$Db1_{2} O(4_{2}, 2, 649(2))$	S1 02: 1 440(2)	

Pb1a-O1d: 2.704(2)	Pb1a-O3b: 2.771(3)	C1-O1b: 1.259(2)
Pb1a-O1e: 2.704(2)	Pb1a-O4a: 2.648(2)	S1-02: 1.449(3)
Pb1a-O1f: 2.531(2)	Pb1a-O4h: 2.743(3)	S1-03: 1.467(2)
Pb1a-O2g: 2.688(3)		S1-O3b: 1.467(2)

Symmetry transformations used to generate equivalent atoms: (a) -x + 1, y, -z + 1; (b) x, -y + 1, z; (c) x + 0.5, -y + 1.5, z; (d) -x + 1, y, -z + 2; (e) -x + 1, -y + 1, -z + 2; (f) x + 0.5, y - 0.5, z; (g) -x + 1, -y + 1, -z + 1; (h) x + 1, y, z + 1.

# 4. Conclusions

In summary, we found that during the synthesis of 3,5dimethylpyrazole-4-sulfonic acid by sulfonation of 3,5-dimethylpyrazole by sulfuric acid, the acetic anhydride solvent also undergoes sulfonation. Under the experimental conditions employed, sulfuric acid can sulfonate acetic anhydride (but not acetic acid) to sulfoacetic acid, and also to methanedisulfonic acid in the presence of



**Fig. 4.** View of the packing in  $Ba(SA)(H_2O)$  along the *a* axis, showing the content of the unit cell.



**Fig. 5.** Crystal structure of Pb(SA)( $H_2O$ ), showing the coordination sphere around Pb, as well as the coordination mode of the SA ligand. Symmetry codes: (a) -x + 1, *y*, -z + 1; (b) x, -y + 1, z; (c) x + 0.5, -y + 1.5, z; (d) -x + 1, y, -z + 2; (e) -x + 1, -y + 1, -z + 2; (f) x + 0.5, y - 0.5, z; (g) -x + 1, -y + 1, -z + 1; (h) x + 1, y, z + 1.



Fig. 6. View of the packing in  $Pb(SA)(H_2O)$  along the *b* axis, showing the content of the unit cell.



**Fig. 7.** Crystal structure of Cs<sub>2</sub>(MDS), showing the coordination sphere around Cs. Symmetry codes: (a) x, -y + 1, z + 0.5; (b) -x + 1, -y + 1, -z + 1; (c) x, -y + 1, z - 0.5; (d) -x + 0.5, y + 0.5, -z + 0.5; (e) -x + 0.5, -y + 0.5, -z; (f) x, y + 1, z.

Selected bond lengths (Å)	for Cs <sub>2</sub> (MDS).
$(s_1 - 01 \cdot 3373(5))$	$(s_1 - 0.2c; 3.032(5))$

Table 6

Cs1-01: 3.373(5)	Cs1-O2c: 3.032(5)	Cs1-O3f: 3.286(5)
Cs1-01a: 3.151(5)	Cs1-O2d: 3.051(5)	S1-03: 1.454(5)
Cs1-O1b: 3.126(6)	Cs1-O3d: 3.380(5)	S1-04: 1.455(5)
Cs1-02: 3.026(6)	Cs1-O3e: 3.339(5)	S1-05: 1.462(5)

Symmetry transformations used to generate equivalent atoms: (a) x, -y + 1, z + 0.5; (b) -x + 1, -y + 1, -z + 1; (c) x, -y + 1, z - 0.5; (d) -x + 0.5, y + 0.5, -z + 0.5; (e) -x + 0.5, -y + 0.5, -z; (f) x, y + 1, z.



**Fig. 8.** Crystal structure of  $Cs_2(MDS)$ , showing the coordination mode of the MDS ligand. Symmetry code: (a) -x + 1, y, -z + 0.5.

3,5-dimethylpyrazole. The composition of the solid material reported earlier as pure 3,5-dimethylpyrazole-4-sulfonic acid [6] was found by <sup>1</sup>H NMR analysis to be approximately 47 mol% 3,5-dimethylpyrazole-4-sulfonic acid, 34 mol% sulfoacetic acid and 19 mol% methanedisulfonic acid. Both sulfoacetate and methanedisulfonate ions were also identified in the crystal structures of the corresponding Co<sup>2+</sup>, Zn<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup> and Cs<sup>+</sup> complexes, obtained using the above ligand mixture. Within those crystal structures, the ligands display varying coordination modes and lead to a variety of coordination polymers. For the sulfoacetate ligand, three new coordination modes were observed: µ-sulfonato-1κO-acetato-1κO:2κO',  $\mu_6$ -sulfonato-1κ<sup>2</sup>O,O';2κO:3κO';4κO''-acetato-1:5 $\kappa$ 0;5:6 $\kappa$ 0' and  $\mu_5$ -sulfonato-1 $\kappa^2$ 0,0';2 $\kappa$ 0''-acetato-3:4 $\kappa$ 0;4:5 $\kappa$ 0', as opposed to the published coordination modes of µ-sulfoacetato-1κ0:2κ0′ [11], μ<sub>7</sub>-sulfo-1κ0;2κ0′;3:4κ0″-acetato-1:5κ0;6:7κ0′ [9] and  $\mu_5$ -sulfo-1 $\kappa$ O;2 $\kappa$ O;3:4 $\kappa$ O''-acetic acid-3:5 $\kappa$ O (carboxylic acid group coordinated with the carbonyl O-atom) [10]. We are



Fig. 9. View of the packing in  $Pb(SA)(H_2O)$  along the *c* axis, showing the content of the unit cell

currently working on an improved method of preparing pure 3,5-dimethylpyrazole-4-sulfonic acid; details will be published elsewhere in due course.

# **Appendix A. Supplementary material**

CCDC 861329, 861330, 861331, 861332 and 861333 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.12.022.

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