

Di- μ -sulfito-bis[(4,4'-dimethyl-2,2'-bipyridine)zinc(II)] dihydrate and poly[[aqua(1,10-phenanthroline)-zinc(II)]- μ_3 -sulfito-zinc(II)- μ_3 -sulfito]

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Two different zinc sulfite compounds have been prepared through the decomposition of pyrosulfite–dithionite ions in aqueous solution, *viz.* a dimeric complex, di- μ -sulfito- $\kappa^3 O, O': O''; \kappa^3 O: O', O''$ -bis[(4,4'-dimethyl-2,2'-bipyridine- $\kappa^2 N, N'$)zinc(II)] dihydrate, $[\text{Zn}_2(\text{SO}_3)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$, (I), which was solved and refined from a twinned sample, and an extended polymer, poly[[aqua(1,10-phenanthroline)- $\kappa^2 N, N'$]zinc(II)]- μ_3 -sulfito- $\kappa^2 O: O': O''$ -zinc(II)- μ_3 -sulfito- $\kappa^3 O: O: O'$], $[\text{Zn}_2(\text{SO}_3)_2(\text{C}_{12}\text{H}_{10}\text{N}_2)(\text{H}_2\text{O})]_n$, (II). In (I), the dinuclear Zn^{II} complex has a center of symmetry. The cation is five-coordinate in a square-pyramidal arrangement, the anion fulfilling a bridging chelating role. Compound (II) comprises two different zinc units, one being five-coordinate (square pyramidal) and the other four-coordinate (trigonal pyramidal), and two independent sulfite groups with different binding modes to the cationic centers.

Comment

We have recently commented (Díaz de Vivar *et al.*, 2004) on the feasibility of producing novel thiosulfate complexes of group XII metals, which are otherwise difficult to obtain by conventional methods, through the decomposition of less common sulfur oxoanions, such as dithionite and pyrosulfite. The argument lay in the instability of these anions in aqueous solutions (Remy, 1956), which, when interacting with transition metal ions and organic ligands, can produce a variety of interesting transformation products. Sodium dithionite, for example, which is fairly stable in the solid state, decomposes in solution, yielding pyrosulfite and thiosulfate. On the other hand, the chemistry in solution of the former is similar to that of SO_3^{2-} and HSO_3^- , even though in the solid state, S^{III} and S^{V} are the states to be expected for sulfur.

This high anionic instability (which makes their own chemistry so difficult) makes these anions attractive as precursors. Some previously unintentional outcomes suggested (Harvey *et al.*, 2004) and further intentional synthesis confirmed (Díaz de Vivar *et al.*, 2004) that the method could be an alternative route for obtaining thiosulfate complexes where direct synthesis had previously proven unsuccessful. The present work deals with an extension of this method, as applied to sulfite complexes, another of the anions present in the dithionite–pyrosulfite complex equilibrium system. We present here the pioneering results of these trials, *viz.* the syntheses and crystal structures of the title compounds (I) and (II).

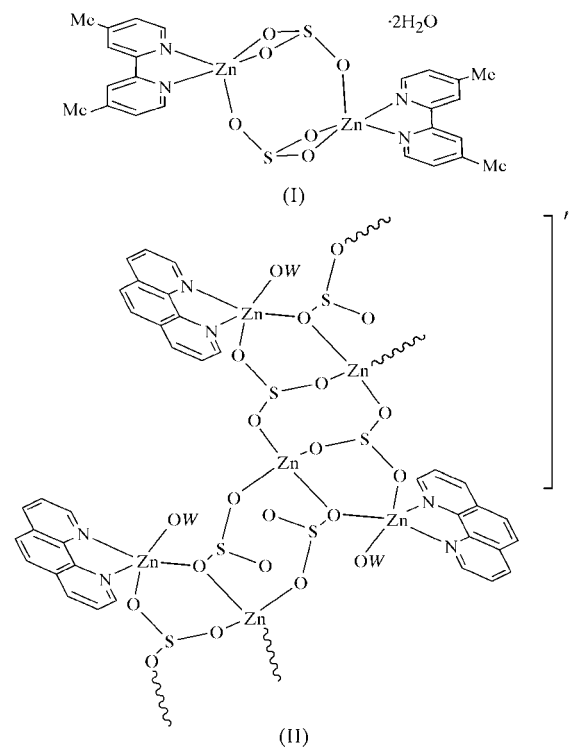


Fig. 1 shows an ellipsoid plot of the dimeric unit in (I); the five-coordinate Zn^{2+} cation is bound to a 4,4'-dimethyl-2,2'-bipyridine unit through its two N atoms and to two symmetry-related sulfite units; one of these forms two bonds in a chelating mode (atoms O2 and O3) and its centrosymmetric counterpart forms a single bond [O1ⁱ; symmetry code: (i) $1 - x, 1 - y, 1 - z$; Table 1]. The coordination environment is thus square pyramidal, with the pair of chelating ligands

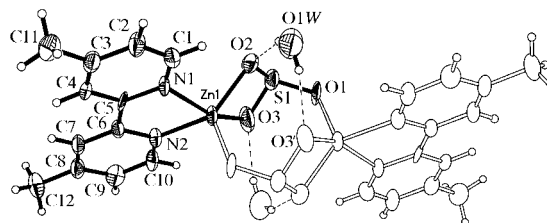


Figure 1
An XP diagram (Sheldrick, 1994) of the dimeric unit in (I). The independent moiety is drawn with full (50% probability) displacement ellipsoids. Intramolecular hydrogen bonds are shown as broken lines. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

defining the base [maximum deviation 0.15 (1) Å for both O atoms and the cation lying 0.63 (1) Å out of the basal plane, towards the apex. This is occupied by atom O1ⁱ, with a Zn–O vector shifted *ca* 10° from the normal to the plane. The two Zn²⁺ cations are then connected by two bridges (simple on one

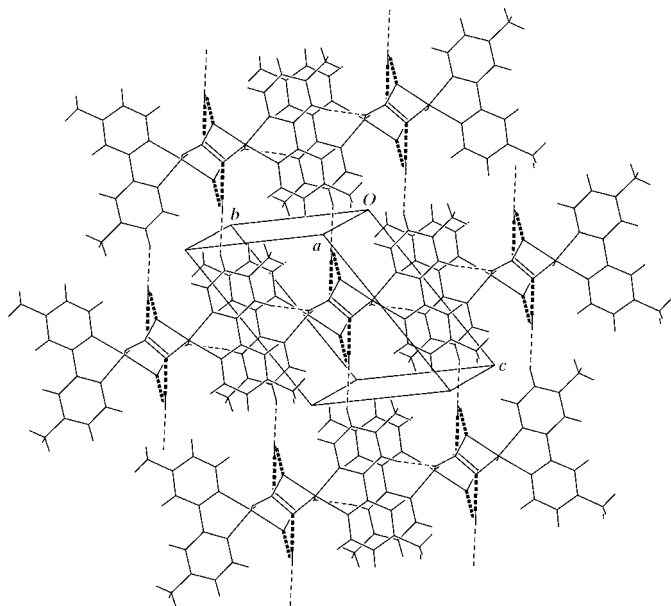


Figure 2

A packing diagram of (I), parallel to (110), showing the non-bonding interactions. Thick broken lines indicate intradimeric interactions involving the water H atoms; thin broken lines indicate C–H...O interactions connecting dimers. Superposed 4,4'-dimethyl-2,2'-bipyridine groups provide out-of-plane π – π interactions.

side and double on the other), the Znⁱ··Znⁱ distance being 3.943 (1) Å. There is also an intradimeric hydrogen-bonding interaction linking atoms O2 and O3ⁱ *via* atom O1W (Table 2 and Fig. 1). The remaining (and weaker) non-bonding contacts stabilize the structure in three orthogonal directions; the two C–H···O interactions, at right angles to one another, connect dimers in the (110) plane into two-dimensional structures (Table 2 and Fig. 2). These broad 'planes', in turn, are connected by π – π contacts between centrosymmetrically related (and therefore strictly parallel) aromatic groups. Table 3 provides some relevant features of these interactions.

Structure (II) comprises instead two independent zinc centers, connected by two non-equivalent sulfite units to form polymeric chains running along the *a* axis (Fig. 3). One of the cationic centers (Zn1²⁺) is five-coordinate in the form of a square pyramid; the basal plane is defined by atoms N1 and N2 of a chelating phenanthroline group, an O atom from one of the sulfite units (O1B) and one aqua O atom (O1W). The least-squares basal plane has a mean deviation of 0.034 Å, and the cation lies 0.60 (1) Å from the plane, towards the apex. This is occupied by an O atom from the second sulfite group [O3A–Zn1 = 1.968 (3) Å, the shortest bond in the polyhedron] at 8° from the normal to the plane. The second cation (Zn2²⁺) is four-coordinate in a trigonal-pyramidal geometry formed by two O atoms from each of the sulfite groups, *viz.* atoms O2A', O1B and O2B'' defining the base and atom O1A the apex [symmetry codes: (') $-x, 2 - y, -z$; (') $1 - x, 2 - y, -z$]. It is the very small deviation of the three apical angles [range 101.1 (1)–101.5 (1)°; Table 4] that favors a trigonal-pyramidal instead of, say, a tetrahedral description. The apical vector deviates just 0.6° from the normal to the plane. The two

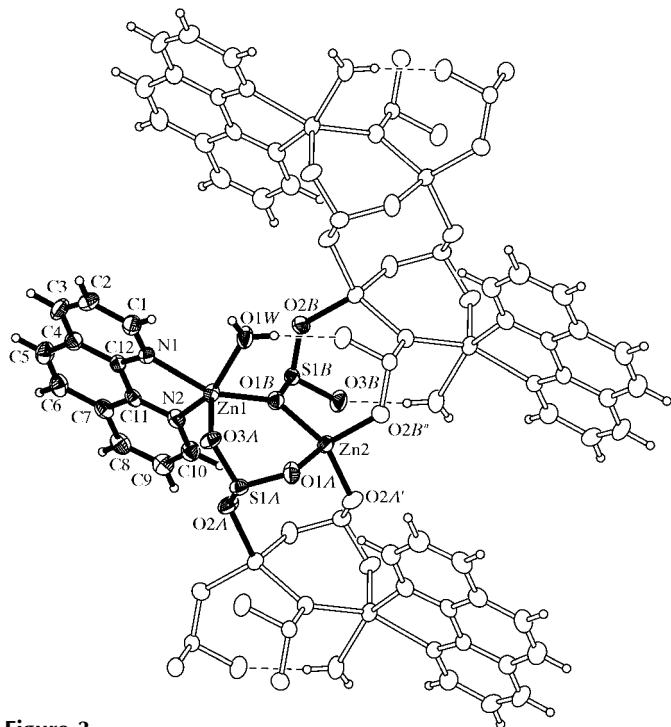


Figure 3

An XP diagram (Sheldrick, 1994) of the polymeric chain in (II). The independent part is represented by full (50% probability) displacement ellipsoids. Intrachain hydrogen bonds are shown as broken lines. [Symmetry codes: (') $-x, 2 - y, -z$; (') $1 - x, 2 - y, -z$.]

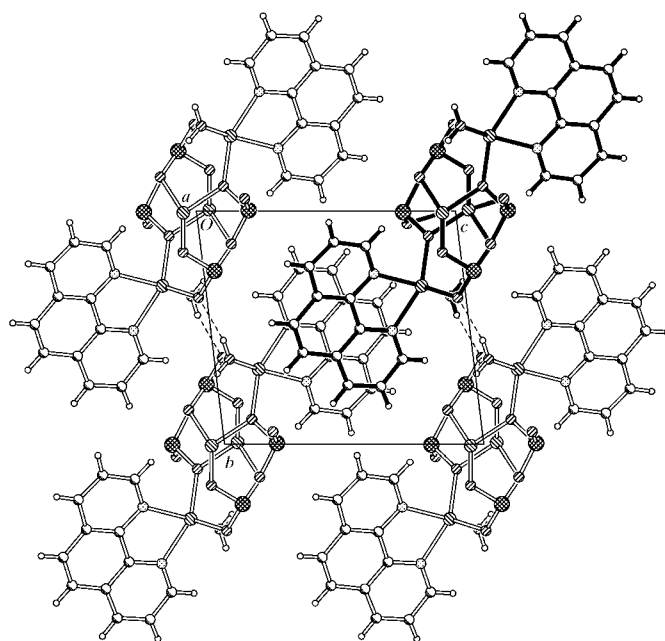


Figure 4

A packing diagram of (II), along the chain direction, showing the way in which planes are built up and the hydrogen-bonding interactions; the superposed phenanthroline groups providing the π – π contacts between chain groups are shown at the center of the figure. One of these chains has been highlighted for clarity.

independent sulfite anions coordinate in diverse ways and this diversity is reflected in their internal geometry. Thus, unit *A*, which binds to each O atom attached to one and only one cationic center, exhibits a rather even distribution of S—O distances (Table 4). Unit *B*, on the other hand, exhibits the largest span, with a clear inverse correspondence between coordination involvement and S—O bond lengths. Thus, atom O1*B*, which binds to two metal ions, forms the longest S—O bond; atom O2*B*, with its single bond to a Zn atom, forms an intermediate-length bond and atom O3*B*, which does not coordinate at all, is the closest to the S atom.

The unit so far described is the elemental link of a column evolving along (100) in the form of a double chain or strip, into which the symmetry centers along the *a* axis appear embedded. These chains fit into one another in a gear-like fashion, forming planes parallel to (011) (Fig. 4), in which the internal cohesion is provided by the π – π contact between phen groups (Table 6), as well as by one hydrogen bond (Table 5) through H1*WA* from the aqua molecule. The remaining hydrogen contact (through H1*WB*) helps in linking neighboring planes together.

Experimental

Both compounds were obtained by dissolving the corresponding aromatic amine [4,4'-dimethyl-2,2'-bipyridine for (I) and phenanthroline monohydrate for (II)] in ethanol (96%) and allowing this solution to diffuse slowly into an aqueous solution of zinc acetate dihydrate, Na₂S₂O₄·2H₂O and K₂S₂O₅ (molar ratios 1:1:2). After two months, crystals of a suitable size for X-ray analysis had developed.

Compound (I)

Crystal data

[Zn₂(SO₃)₂(C₁₂H₁₂N₂)]·2H₂O
M_r = 695.36
 Triclinic, *P* $\bar{1}$
a = 7.534 (4) Å
b = 9.621 (5) Å
c = 11.051 (5) Å
 α = 113.233 (8)°
 β = 96.932 (9)°
 γ = 106.746 (9)°
V = 679.4 (6) Å³

Z = 1
D_x = 1.700 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 273 reflections
 θ = 4.0–25.5°
 μ = 1.98 mm⁻¹
T = 296 (2) K
 Blocks, colorless
 0.22 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan [SADABS (Sheldrick, 1996) in SAINT-NT (Bruker, 2000)]
T_{min} = 0.66, *T_{max}* = 0.82
 2037 measured reflections

2037 independent reflections
 1623 reflections with *I* > 2σ(*I*)
R_{int} = 0.079
 θ_{\max} = 27.6°
h = -9 → 9
k = -11 → 11
l = 0 → 14

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.064
wR (*F*²) = 0.182
S = 1.01
 2037 reflections
 191 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.1397P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.011$
 $\Delta\rho_{\max} = 0.95 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.30 \text{ e \AA}^{-3}$

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

Zn1—O1 ⁱ	1.951 (4)	Zn1—O3	2.198 (5)
Zn1—O2	2.022 (4)	S1—O3	1.514 (5)
Zn1—N2	2.049 (5)	S1—O1	1.522 (5)
Zn1—N1	2.110 (5)	S1—O2	1.532 (5)
O1 ⁱ —Zn1—O2	121.9 (2)	N2—Zn1—N1	78.6 (2)
O1 ⁱ —Zn1—N2	102.8 (2)	O1 ⁱ —Zn1—O3	107.4 (2)
O2—Zn1—N2	134.7 (2)	O2—Zn1—O3	66.9 (2)
O1 ⁱ —Zn1—N1	99.3 (2)	N2—Zn1—O3	94.9 (2)
O2—Zn1—N1	99.28 (19)	N1—Zn1—O3	153.3 (2)

Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1 <i>W</i> —H1 <i>WB</i> ···O3 ⁱ	0.83 (8)	2.06 (7)	2.823 (10)	155 (6)
O1 <i>W</i> —H1 <i>WA</i> ···O2	0.82 (5)	2.07 (6)	2.835 (10)	157 (6)
C7—H7···O1 ⁱⁱ	0.93	2.46	3.247 (7)	142
C9—H9···O1 <i>W</i> ⁱⁱⁱ	0.93	2.49	3.374 (9)	159

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

Table 3
 π – π contacts (Å, °) for (I).

Group 1/group 2	ipd (Å)	ccd (Å)	sa (°)
Ring <i>B</i> '/ring <i>A</i>	3.46 (1)	3.69 (1)	20.4 (2)
Ring <i>B</i> ''/ring <i>A</i>	3.49 (1)	3.86 (1)	25.3 (2)
Ring <i>A</i> '/ring <i>B</i>	3.55 (1)	3.69 (1)	15.9 (2)
Ring <i>A</i> ''/ring <i>B</i>	3.60 (1)	3.86 (1)	20.9 (2)

Notes: ring *A* involves atoms N1 and C1–C5; ring *B* involves atoms N2 and C6–C10. Symmetry codes: (') 2 - *x*, 2 - *y*, 1 - *z*; (')' 1 - *x*, 2 - *y*, 1 - *z*. ipd is the interplanar distance (distance from one plane to the neighboring centroid), ccd is the center-to-center distance (distance between ring centroids) and sa is the slippage angle (angle subtended by the intercentroid vector to the plane normal); for details, see Janiak (2000).

Compound (II)

Crystal data

[Zn₂(SO₃)₂(C₁₂H₁₀N₂)(H₂O)]
M_r = 489.08
 Triclinic, *P* $\bar{1}$
a = 8.0271 (16) Å
b = 9.4817 (19) Å
c = 10.286 (2) Å
 α = 80.98 (3)°
 β = 80.39 (3)°
 γ = 75.55 (3)°
V = 742.0 (3) Å³
Z = 2
D_x = 2.189 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10.2–16.0°
 μ = 3.56 mm⁻¹
T = 293 (2) K
 Plates, colorless
 0.32 × 0.24 × 0.14 mm

Data collection

Rigaku AFC-6S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.37, *T_{max}* = 0.60
 3847 measured reflections
 2926 independent reflections
 1976 reflections with *I* > 2σ(*I*)

R_{int} = 0.034
 θ_{\max} = 26.0°
h = -9 → 9
k = -11 → 2
l = -12 → 12
 3 standard reflections
 every 150 reflections
 intensity decay: 1.2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.079$
 $S = 0.97$
 2926 reflections
 232 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.039P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.029$
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$

Table 4
 Selected geometric parameters (\AA , $^\circ$) for (II).

Zn1—O3A	1.968 (3)	Zn2—O1A	2.007 (3)
Zn1—O1B	2.037 (3)	S1A—O1A	1.523 (3)
Zn1—N1	2.110 (3)	S1A—O2A	1.528 (3)
Zn1—O1W	2.136 (3)	S1A—O3A	1.546 (3)
Zn1—N2	2.152 (3)	S1B—O3B	1.489 (3)
Zn2—O2A ^{iv}	1.951 (3)	S1B—O2B	1.520 (3)
Zn2—O2B ^v	1.955 (3)	S1B—O1B	1.583 (3)
Zn2—O1B	2.002 (3)		
O3A—Zn1—O1B	106.21 (11)	O1W—Zn1—N2	150.99 (14)
O3A—Zn1—N1	107.63 (13)	O2A ^{iv} —Zn2—O2B ^v	103.79 (12)
O1B—Zn1—N1	146.14 (13)	O2A ^{iv} —Zn2—O1B	128.31 (12)
O3A—Zn1—O1W	96.47 (13)	O2B ^v —Zn2—O1B	115.87 (12)
O1B—Zn1—O1W	85.31 (12)	O2A ^{iv} —Zn2—O1A	101.47 (13)
N1—Zn1—O1W	89.82 (12)	O2B ^v —Zn2—O1A	102.19 (12)
O3A—Zn1—N2	112.27 (13)	O1B—Zn2—O1A	101.07 (12)
O1B—Zn1—N2	90.22 (12)	Zn2—O1B—Zn1	121.27 (14)
N1—Zn1—N2	78.10 (13)		

Symmetry codes: (iv) $-x, 2 - y, -z$; (v) $1 - x, 2 - y, -z$.

Table 5
 Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA \cdots O3A ^{vi}	0.82 (4)	2.06 (4)	2.873 (4)	168 (4)
O1W—H1WB \cdots O3B ^v	0.82 (4)	1.93 (4)	2.750 (4)	173 (4)

Symmetry codes: (v) $1 - x, 2 - y, -z$; (vi) $1 - x, 1 - y, -z$.

Table 6
 π - π contacts (\AA , $^\circ$) for (II).

Group 1/group 2	ipd (\AA)	ccd (\AA)	sa ($^\circ$)
Rings A'B'/rings AB	3.50 (1)	3.52 (1)	10.0 (2)
Rings B'C'/rings BC	3.34 (1)	3.55 (1)	18.5 (2)

Notes: rings AB involve atoms N1, C1–C7, C11 and C12; rings BC involve atoms N2 and C4–C12. Symmetry codes: (') $1 - x, 1 - y, 1 - z$; (") $-x, 1 - y, 1 - z$. ipd is the interplanar distance (distance from one plane to the neighboring centroid), ccd is the center-to-center distance (distance between group centroids) and sa is the slippage angle (angle subtended by the intercentroid vector to the plane normal); for details, see Janiak (2000).

Crystals of (I) grew as non-merohedral twins, a fact that was clearly visible with the CCD at the data collection stage. Even though the (two) most important orientations could be separated and non-overlapped reflections integrated, heavily overlapped reflections were impossible to deal with. Since their inclusion impaired the

refinement, it was decided to omit them from the data set, considering that in spite of this drawback a very reasonable data-to-parameter ratio of 10:1 could still be obtained, with an even distribution of data in reciprocal space. The only suspicious outcome attributable to poor data quality was the abnormally prolate displacement ellipsoids for atoms C5 and O1. The twin ratio in the crystal measured was about 70:30. H atoms attached to C atoms and unambiguously defined by the stereochemistry were placed at calculated positions ($C-H = 0.93 \text{ \AA}$) and allowed to ride. Terminal methyl groups ($C-H = 0.96 \text{ \AA}$) were also allowed to rotate. $U_{\text{iso}}(H)$ values were set at $1.2U_{\text{eq}}$ (parent atom) or $1.5U_{\text{eq}}(C_{\text{methyl}})$. H atoms of water molecules were located from difference Fourier syntheses and refined with restrained parameters [$O-H = 0.82 (1) \text{ \AA}$ and $H\cdots H = 1.35 (2) \text{ \AA}$].

For compound (I), data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*. For compound (II), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*. For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP in SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1207). Services for accessing these data are described at the back of the journal.

References

Bruker (2000). *SAINT-NT*. Version 6.02a. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2001). *SMART-NT*. Version 5.624. Bruker AXS Inc., Madison, Wisconsin, USA.
 Díaz de Vivar, E., Baggio, E. & Baggio, R. (2004). *Acta Cryst.* **C60**, m495–m497.
 Harvey, M., Baggio, S., Pardo, H. & Baggio, R. (2004). *Acta Cryst.* **C60**, m79–m81.
 Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3898.
 Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Remy, H. (1956). In *Treatise on Inorganic Chemistry*. Amsterdam: Elsevier.
 Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.