$\theta$–$2\theta$ scans

Absorption correction:
 $\psi$ scan (XEMP; Siemens, 1991)
 $T_{min} = 0.60$, $T_{max} = 0.66$
8507 measured reflections
6945 independent reflections

$R_{int} = 0.0575$
$\theta_{max} = 30°$
$h = -1 \rightarrow 15$
$k = -1 \rightarrow 19$
$l = -21 \rightarrow 21$
3 standard reflections
 every 97 reflections
 intensity decay: none

### Refinement

Refinement on $F^2$
$R(F) = 0.047$
$wR(F^2) = 0.104$
$S = 0.852$
6945 reflections
252 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F) + (0.0008)F^2]$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.578$ e Å$^{-3}$
$\Delta\rho_{min} = -0.720$ e Å$^{-3}$
Extinction correction: SHELXL97
Extinction coefficient: 0.00012 (7)
Scattering factors from International Tables for Crystallography (Vol. C)

### Table 3. Selected bond lengths (Å) for (III)

| | | | |
|---|---|---|---|
| I1—Cu6 | 2.552 (2) | I3—Cu5$^i$ | 2.562 (2) |
| I1—Cu7 | 2.568 (2) | I3—Cu6$^i$ | 2.571 (2) |
| I1—Cu4 | 2.579 (2) | Na1—O21 | 2.257 (7) |
| I1—Cu5 | 2.588 (2) | Na1—O22 | 2.279 (3) |
| I2—Cu6$^i$ | 2.545 (2) | Na1—O1 | 2.564 (6) |
| I2—Cu5 | 2.551 (2) | Na1—O4 | 2.628 (7) |
| I2—Cu7$^i$ | 2.568 (2) | Na1—O16 | 2.663 (7) |
| I2—Cu4 | 2.593 (2) | Na1—O10 | 2.839 (7) |
| I3—Cu4 | 2.5217 (19) | Na1—O7 | 2.886 (7) |
| I3—Cu7 | 2.538 (2) | Na1—O13 | 2.897 (7) |

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

Extinction was refined for all three structures but was minimal. Atoms Cu1–Cu4 in (I) and (II), and atoms Cu4–Cu7 in (III) all have 50% site occupancy.

For all compounds, data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1990)

## References

Bowmaker, G. A., Clark, G. R. & Yuen, D. K. P. (1976). J. Chem. Soc. Dalton Trans. pp. 2329–2351.
Caulton, K. G., Davies, G. & Holt, E. M. (1990). Polyhedron, pp. 2319–2351.
Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T. A., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challalcombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andrews, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. L., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. & Pople, J. A. (1995). GAUSSIAN94. Revision A1. Gaussian Inc., Pittsburgh, PA, USA.
Hu, G. & Holt, E. M. (1994a). Acta Cryst. C50, 1212–1214.
Hu, G. & Holt, E. M. (1994b). Acta Cryst. C50, 1576–1578.
Hu, G. & Holt, E. M. (1994c). Acta Cryst. C50, 1578–1580.

Hu, G. & Holt, E. M. (1994d). Acta Cryst. C50, 1890–1892.
Hu, G., Mains, G. J. & Holt, E. M. (1995). Inorg. Chim. Acta, 240, 559–565.
Jagner, S. & Helgesson, G. (1991). Advances in Inorganic Chemistry, edited by A. G. Syles, Vol. 37, pp. 1–45. San Diego: Academic Press.
Jouini, N., Guen, L. & Tournoux, M. (1980). Rev. Chem. Miner. 17, 486–492.
Nurtaeva, A. & Holt, E. M. (1998a). Acta Cryst. C54, 594–597.
Nurtaeva, A. & Holt, E. M. (1998b). Acta Cryst. C54, 597–600.
Rath, N. P. & Holt, E. M. (1985). J. Chem. Soc. Chem. Commun. pp. 665–667.
Rath, N. P., Holt, E. M. & Tanimura, K. (1985). Inorg. Chem. 24, 3934–3938.
Shannon, R. D. (1976). Acta Cryst. A32, 751–754.
Sheldrick, G. M. (1990). Acta Cryst. A46, 467–473.
Sheldrick, G. M. (1997). SHELXL97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
Siemens (1990). XP. Interactive Molecular Graphics Program. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1991). XSCANS User's Manual. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tompkins, J. A., Maxwell, J. L. & Holt, E. M. (1987). Inorg. Chim. Acta, 127, 1–7.

# Tetraaqua(2,2'-bipyridyl-N,N')cadmium(II) sulfate and catena-poly[[[diaqua(2,2'-bipyridyl-N,N')cadmium(II)]-$\mu$-(sulfato-O:O')] hydrate]

MIGUEL HARVEY,[a] SERGIO BAGGIO,[b] RICARDO BAGGIO[c] AND ALVARO MOMBRÚ[d]

[a] Universidad Nacional de la Patagonia, Sede Trelew, 9100 Trelew, and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, [b] Universidad Nacional de la Patagonia, Sede Puerto Madryn, and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, [c] Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, and [d] CSSC Lab., Facultad de Química, Universidad de la República, Montevideo, Uruguay. E-mail: baggio@cnea.gov.ar

## Abstract

In both title compounds, [Cd(C$_{10}$H$_8$N$_2$)(H$_2$O)$_4$]SO$_4$, (I), and [Cd(SO$_4$)(C$_{10}$H$_8$N$_2$)(H$_2$O)$_2$]·H$_2$O, (II), the Cd$^{II}$ ion is octahedrally coordinated. In (I), the Cd$^{2+}$ ion is coordinated to a bipyridine and four water molecules, the structure being monomeric and strictly ionic in nature, and in (II), to a bipyridine, two water molecules

and two O atoms from two translationally related sulfate groups, thus defining polymeric chains along the unique crystallographic *b* axis.

## Comment

The structural chemistry of divalent metals complexed with sulfur oxoanions has been of interest to us in the last few years. The case of $Cd^{2+}$, in particular, deserves special attention since the characteristics of the metal, with its complete *d* shell, and the properties of ligands such as thiosulfate, sulfite and sulfate, give rise to an interesting variety of patterns of coordination around the metal ion. In the case of the sulfate complexes, both monodentate as well as bridging modes of coordination of the ligand (through two or three O atoms) have been reported (Rahmani *et al.*, 1996, and references therein). In the present paper, we report the structures of two closely related cadmium–sulfate compounds, namely tetraaqua(2,2'-bipyridyl-*N*,*N'*)cadmium(II) sulfate, (I), and *catena*-poly[[[diaqua(2,2'-bipyridyl-*N*,*N'*)-cadmium(II)]-μ-(sulfato-*O*:*O'*)] hydrate], (II), which appear in the same synthesis process, and interconvert [(II) into (I)] on standing in contact with the mother liquor.
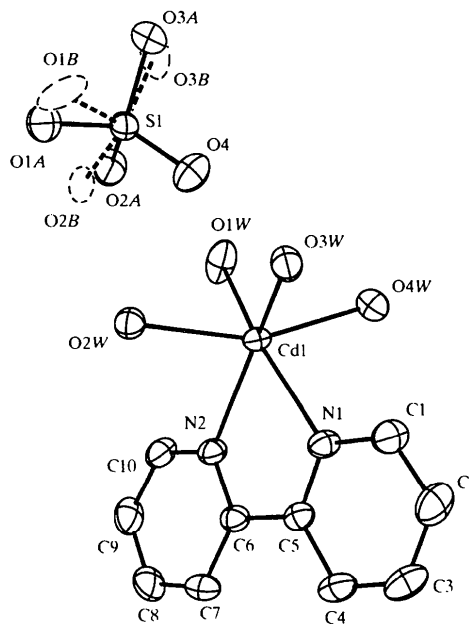


Fig. 1. The structure of (I) showing the numbering scheme used and displacement ellipsoids at the 40% probability level. The rotational disorder present in the ionic sulfate group along the S1—O4 bond has been represented by drawing in full line those sites with larger occupancies.

Compound (I) is monomeric and strictly ionic in nature (Fig. 1). The anionic role is fulfilled by an isolated sulfate group, with rotational disorder along one of the S—O bonds, presenting two main orientations with an occupation ratio of 3:1. The $Cd^{2+}$ ion, in turn, is coordinated to a bidentate bipyridine molecule through its two N atoms and to four water molecules which define an octahedral environment with a narrow spread of coordination distances [range: 2.246 (3)–2.345 (2) Å], but with a large angular deviation from ideal values; *viz* those angles expected to be 90° range from 70.7 (1) to 114.7 (1)° and those expected to be 180° range from 147.8 (1) to 157.9 (1)° (Table 1). The two charged entities interact strongly through a dense network of hydrogen bonding (Table 2), where all the H atoms of the coordinated water molecules take part, as well as all the O atoms of the anion. The latter seem to be highly interactive, as some short contacts involving bipyridine H atoms are also noticeable.

In structure (II), there are two crystallographically independent but very similar chains parallel to **b**. Each is composed of Cd octahedra in which the sulfate

O atoms occupy apical sites and the sulfate groups link neighboring Cd atoms along **b** (Fig. 2). The equatorial sites around cadmium are occupied by two bipyridyl N atoms and by two water molecules. The bidentate ligand imposes constraints on the angles around cadmium similar to those in (I), but the octahedra in (II) are otherwise less distorted than those in (I), as shown by the ranges of angles equivalent to those given for (I) above: molecule *A*, 72.2 (2)–97.5 (2) and 165.1 (2)–176.5 (2)°, and molecule *B*, 71.5 (2)–95.9 (2) and 161.2 (2)–178.8 (2)°. The two chains are related approximately by a symmetry center at $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$, but a least-squares fit of one chain onto the other showed an r.m.s. deviation in atom positions of 0.35 Å and a maximum of 0.65 Å (between C2 and C9 of the bipyridyl ligands).

In molecules *A* and *B* of (II), the sulfate ion is quite regular. Similar geometries have been found in other cadmium sulfate-bridged complexes (Caira *et al.*, 1976; Rodesiler *et al.*, 1987), but it seems to oppose a rather general trend observed in similarly coordinated sulfates bridging a variety of other cations. A search in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) suggested that there is a tendency towards lengthening of the S—O bonds to the coordinated O atoms, as shown by the ratio S—$O_{coord}$/S—$O_{non-coord}$; in over 41 cases with $R < 0.07$, this ratio averaged 1.034 (5).
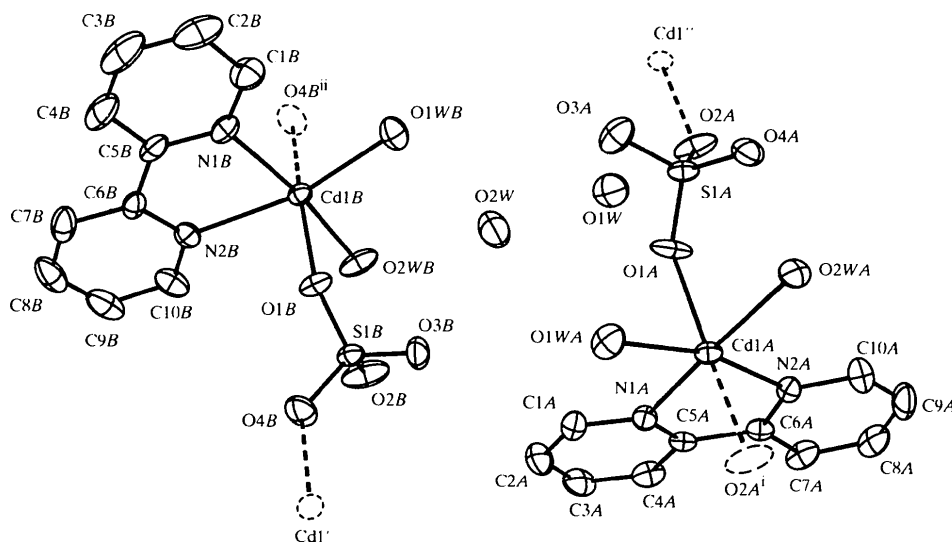
Fig. 2. The structure of (II) showing the numbering scheme used and displacement ellipsoids at the 40% probability level. The way in which the two independent polymeric chains develop is suggested.

Although not all H atoms have been located (see *Experimental* and Table 4), the intermolecular distances suggest strong hydrogen bonding between the chains.

## Experimental

Compounds (I) and (II) appeared at different stages of crystallization of the same starting preparation. This consisted of a mixture of an ethanolic solution of bipyridine and an aqueous solution of cadmium sulfate in a 1:1 molar ratio. Upon concentration, this preparation resulted in a gel. The latter was dissolved in boiling water and the resulting solution allowed to evaporate for *ca* three weeks, when a crop of needles of compound (II) began to appear. At the later stages of crystallization, a few small equidimensional prisms of phase (I) began to grow. Through a steady digestion of the earlier crystallized solid and subsequent conversion into crystals of the new ionic phase, the latter ended up appearing as the exclusive stable product at large solute concentration.

### Compound (I)

*Crystal data*

[Cd(C$_{10}$H$_8$N$_2$)(H$_2$O)$_4$]SO$_4$
$M_r$ = 436.71
Monoclinic
$P2_1/c$
$a$ = 10.262 (2) Å
$b$ = 12.073 (2) Å
$c$ = 12.357 (3) Å
$\beta$ = 92.47 (3)°
$V$ = 1529.5 (5) Å$^3$
$Z$ = 4
$D_x$ = 1.90 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 7.5–15.0°
$\mu$ = 1.60 mm$^{-1}$
$T$ = 293 (2) K
Prism
0.25 × 0.20 × 0.16 mm
Colorless

*Data collection*

Rigaku AFC-7S diffractometer
$\omega/2\theta$ scans
Absorption correction:
  $\psi$ scan (Molecular Structure Corporation, 1988)
  $T_{min}$ = 0.71, $T_{max}$ = 0.77
3717 measured reflections
3527 independent reflections

2916 reflections with
$I > 2\sigma(I)$
$R_{int}$ = 0.035
$\theta_{max}$ = 27.51°
$h$ = 0 → 13
$k$ = 0 → 15
$l$ = −16 → 16
3 standard reflections
  every 150 reflections
  intensity decay: <2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.095
$S$ = 1.046
3527 reflections
263 parameters
H atoms treated by a
  mixture of independent
  and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ < 0.01
$\Delta\rho_{max}$ = 0.914 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.895 e Å$^{-3}$
Extinction correction:
  SHELXL97
Extinction coefficient:
  0.010 (1)
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. *Selected bond lengths (Å) for (I)*

| | | | |
|---|---|---|---|
| Cd1—O1W | 2.246 (3) | S1—O2B | 1.456 (6) |
| Cd1—O3W | 2.255 (3) | S1—O3A | 1.465 (4) |
| Cd1—N1 | 2.332 (3) | S1—O1A | 1.463 (4) |
| Cd1—N2 | 2.334 (3) | S1—O4 | 1.471 (2) |
| Cd1—O4W | 2.334 (3) | S1—O2A | 1.481 (3) |
| Cd1—O2W | 2.345 (2) | S1—O1B | 1.498 (7) |
| S1—O3B | 1.444 (6) | | |

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

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| O1W—H1WA⋯O1B$^i$ | 0.80 (6) | 1.88 (6) | 2.680 (15) | 170 (6) |
| O1W—H1WA⋯O1A$^i$ | 0.80 (6) | 1.88 (6) | 2.681 (6) | 169 (6) |
| O1W—H1WB⋯O1A$^{ii}$ | 0.80 (4) | 1.97 (4) | 2.751 (6) | 162 (4) |

| | | | | |
|---|---|---|---|---|
| O1W—H1W*B*···O2*B*ⁱⁱ | 0.80 (4) | 2.12 (4) | 2.75 (2) | 135 (3) |
| O2W—H2W*A*···O4ⁱ | 0.75 (3) | 2.08 (3) | 2.845 (4) | 177 (3) |
| O2W—H2W*B*···O2*A* | 0.77 (3) | 1.98 (3) | 2.735 (5) | 164 (3) |
| O2W—H2W*B*···O2*B* | 0.77 (3) | 1.96 (4) | 2.722 (14) | 165 (3) |
| O3W—H3W*A*···O3*A*ⁱⁱⁱ | 0.78 (3) | 1.90 (2) | 2.688 (6) | 170 (2) |
| O3W—H3W*A*···O3*B*ⁱⁱⁱ | 0.78 (3) | 1.85 (3) | 2.636 (15) | 172 (3) |
| O3W—H3W*B*···O4 | 0.77 (4) | 1.95 (4) | 2.717 (4) | 166 (4) |
| O4W—H4W*B*···O2*B*ⁱⁱ | 0.76 (4) | 2.03 (5) | 2.722 (15) | 150 (4) |
| O4W—H4W*A*···O2*A*ⁱⁱ | 0.76 (4) | 2.01 (4) | 2.764 (5) | 165 (4) |
| O4W—H4W*A*···O3*B*ⁱⁱⁱ | 0.77 (3) | 2.42 (3) | 3.15 (2) | 157 (2) |
| O4W—H4W*A*···O3*A*ⁱⁱⁱ | 0.77 (3) | 1.95 (3) | 2.703 (6) | 162 (3) |
| C4—H4*A*···O1*B*ⁱᵛ | 0.93 | 2.24 | 3.160 (15) | 169 |

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

## Compound (II)

### Crystal data

[Cd(SO₄)(C₁₀H₈N₂)(H₂O)₂]·H₂O
$M_r = 418.69$
Monoclinic
$P2_1/c$
$a = 20.998$ (4) Å
$b = 6.823$ (1) Å
$c = 20.001$ (4) Å
$\beta = 94.88$ (3)°
$V = 2855.1$ (9) Å³
$Z = 8$
$D_x = 1.948$ Mg m⁻³
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–15.0°$
$\mu = 1.71$ mm⁻¹
$T = 293$ (2) K
Needle
$0.40 \times 0.18 \times 0.16$ mm
Colorless

### Data collection

Rigaku AFC-7S diffractometer
$\omega/2\theta$ scans
Absorption correction:
  $\psi$ scan (Molecular Structure Corporation, 1988)
  $T_{min} = 0.61$, $T_{max} = 0.75$
6739 measured reflections
6544 independent reflections

4224 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.50°$
$h = -27 \rightarrow 27$
$k = -8 \rightarrow 0$
$l = 0 \rightarrow 25$
3 standard reflections every 150 reflections
  intensity decay: <2%

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.119$
$S = 1.016$
6544 reflections
408 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.086P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 0.681$ e Å⁻³
$\Delta\rho_{min} = -0.866$ e Å⁻³
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected bond lengths (Å) for (II)*

| | | | |
|---|---|---|---|
| Cd1*A*—O1W*A* | 2.277 (5) | Cd1*B*—O2W*B* | 2.225 (5) |
| Cd1*A*—O2W*A* | 2.288 (4) | Cd1*B*—O1W*B* | 2.280 (5) |
| Cd1*A*—N1*A* | 2.287 (4) | Cd1*B*—N1*B* | 2.301 (5) |
| Cd1*A*—O2*A*ⁱ | 2.293 (4) | Cd1*B*—O4*B*ⁱⁱ | 2.314 (4) |
| Cd1*A*—N2*A* | 2.299 (5) | Cd1*B*—N2*B* | 2.331 (5) |
| Cd1*A*—O1*A* | 2.332 (4) | Cd1*B*—O1*B* | 2.345 (4) |
| S1*A*—O1*A* | 1.461 (4) | S1*B*—O2*B* | 1.460 (5) |

| | | | |
|---|---|---|---|
| S1*A*—O2*A* | 1.463 (4) | S1*B*—O3*B* | 1.463 (4) |
| S1*A*—O4*A* | 1.471 (5) | S1*B*—O4*B* | 1.474 (5) |
| S1*A*—O3*A* | 1.475 (5) | S1*B*—O1*B* | 1.474 (4) |

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

Table 4. *Contact distances (Å) for (II)*

| | | | |
|---|---|---|---|
| O1W*A*···O3*A*ⁱ | 2.776 (7) | O2W*B*···O2*B* | 2.667 (7) |
| O1W*A*···O1W | 2.689 (7) | O2W*B*···O4*A*ⁱᵛ | 2.713 (6) |
| O1W*B*···O2W | 2.708 (9) | O1W···O3*A* | 2.907 (7) |
| O1W*B*···O3*B*ⁱⁱ | 2.765 (8) | O1W···O4*B*ⁱⁱⁱ | 2.924 (7) |
| O2W*A*···O4*A* | 2.651 (7) | O2W···O3*A* | 2.991 (8) |
| O2W*A*···O2*B*ⁱⁱⁱ | 2.812 (8) | O2W···O3*B* | 2.833 (7) |

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

In the case of the disordered sulfate anion in (I), soft metric restraints were applied to the S—O and O—O distances so as to ensure a meaningful geometry. H atoms attached to carbon and unequivocally defined by the stereochemistry were placed at their calculated positions and allowed to ride on their host atoms (C—H = 0.96 Å). Water H atoms were located by difference Fourier synthesis and subsequently refined with a restrained O—H distance; in the case of (I), all eight water H atoms were found, while in (II), only seven out of a total of 12 could be located confidently.

For both compounds, 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*; program(s) used to solve structures: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *PARST* (Nardelli, 1983) and CSD (Allen & Kennard, 1993).

## References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Caira, M. R., Nassimbeni, L. R. & Orpen, G. (1976). *Acta Cryst.* **B32**, 140–144.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Rahmani, A., Romero, M. A., Salas, J. M., Quiros, M. & Avarez de Cienfuegos, G. (1996). *Inorg. Chim. Acta*, **247**, 51–55.

Rodesiler, P. F., Charles, N. G., Griffith, E. A. H. & Amma, E. L. (1987). *Acta Cryst.* **C43**, 1058–1061.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.