

Three new Zn^{II} sulfate complexesMiguel Harvey,^a Sergio Baggio,^b Alvaro Mombrú^c and Ricardo Baggio^{d*}

^aUniversidad Nacional de la Patagonia, Sede Trelew, and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, ^bUniversidad Nacional de la Patagonia, Sede Puerto Madryn, and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, ^cCSSC Lab., Facultad de Química, Universidad de la República, Montevideo, Uruguay, and ^dDepartamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: baggio@cnea.gov.ar

Received 10 March 2000

Accepted 28 March 2000

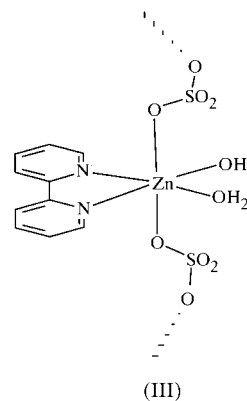
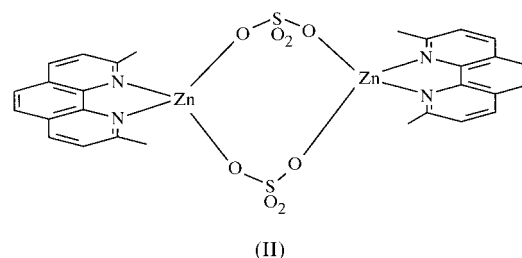
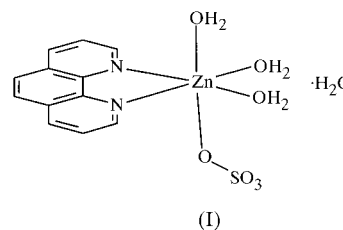
The three zinc sulfate complexes presented herein display three completely different coordination modes, *viz* triaqua(1,10-phenanthroline-*N,N'*)(sulfato-*O*)zinc(II) hydrate, [Zn(SO₄)(C₁₂H₈N₂)(H₂O)₃]·H₂O (octahedral, monomeric), bis(μ-sulfato-*O:O'*)bis[(2,9-dimethyl-1,10-phenanthroline-*N,N'*)zinc(II)], [Zn₂(SO₄)₂(C₁₄H₁₂N₂)₂] (tetrahedral, dimeric), and *catena*-poly[[diaqua(2,2'-bipyridyl-*N,N'*)zinc(II)]-μ-(sulfato-*O:O'*)], [Zn(SO₄)(C₁₀H₈N₂)(H₂O)₂]_n (octahedral, polymeric, twofold crystallographic symmetry). In the first, the sulfate is monodentate, while in the other two it acts as a bidentate bridge between two different Zn centers. There is a variety of sulfate S—O bond lengths, depending on the different coordination conditions and hydrogen-bonding interactions.

Comment

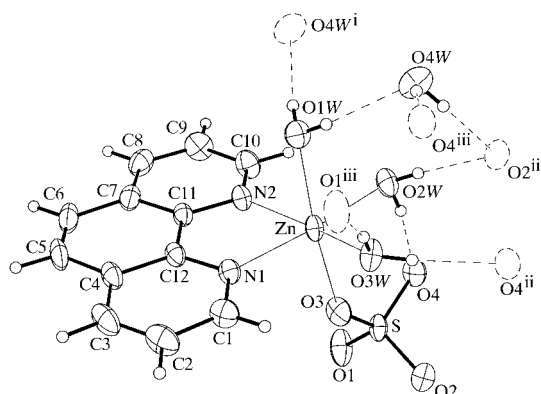
The results of structural studies of Zn^{II} complexes are particularly attractive since, like most *d*¹⁰ metal ions, zinc has the ability to adopt different modes of coordination determined by considerations of size, as well as electrostatic and covalent bonding forces. Furthermore, when complexed with N- and O-donor ligands, its derivatives have an additional importance since such systems are present in some biological molecules of outstanding interest, *viz* phospholipase C (Huogh *et al.*, 1989) and bovine lens leucine aminopeptidase (Burley *et al.*, 1992), *etc.*

The eventual presence of sulfate as a ligand is expected to introduce additional flexibility into the Zn^{II} coordination geometry, due to the versatility of the anion in acting either as a monodentate, bidentate or bridging ligand. A search in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) confirmed this fact, revealing the existence of 23 reported structures, 14 of which are of an ionic nature and nine constitute real sulfato complexes presenting a variety of coordination modes. In five of these complexes, the anion acts

as a simple monodentate ligand in a diversity of Zn^{II} environments, *viz* tetrahedral (Andreotti *et al.*, 1968; Greener *et al.*, 1996), square pyramidal (Zhu *et al.*, 1990) or octahedral (Hanggi *et al.*, 1988; Dubler *et al.*, 1990); in another two compounds it behaves as an *O,O'* bridge in linear polymeric chains of ZnO₆ octahedra (Labadi *et al.*, 1993; Shorsheneva *et al.*, 1994). Finally, in the remaining two, it presents a much more complex coordination, *viz* in (μ₄-sulfido)hexakis(μ₃-sulfido)tris(μ₃-sulfato)nonakis(pyridyl)-decazine trihydrate (Ali *et al.*, 1998), it binds to three different Zn centers as a triply monodentate ligand, fulfilling the role of a multiple link in an extremely intricate three-dimensional network, while in *catena*-[[[(μ₂-4,4'-bipyridyl) aqua(μ₂-sulfato-*O,O',O''*)]zinc hemihydrate] (Songping *et al.*, 1998), it links to two different Zn centers, monocoordinated to one and bicoordinated to the other, also giving rise to a complex structure. Recently, the structure of tetraaqua(1,10-phenanthroline)zinc(II) sulfate hydrate has been reported, in which the anion is not coordinated to the metal (Zhang *et al.*, 1999)



As part of a general structural work on sulfur oxyanions, we report herein the synthesis and structural determination of three novel Zn^{II} sulfate complexes, namely triaqua(1,10-phenanthroline-*N,N'*)(sulfato-*O*)zinc(II) hydrate, (I), bis(μ-sulfato-*O:O'*)bis[(2,9-dimethyl-1,10-phenanthroline)zinc(II)], (II), whose coordination is unprecedented in the literature,

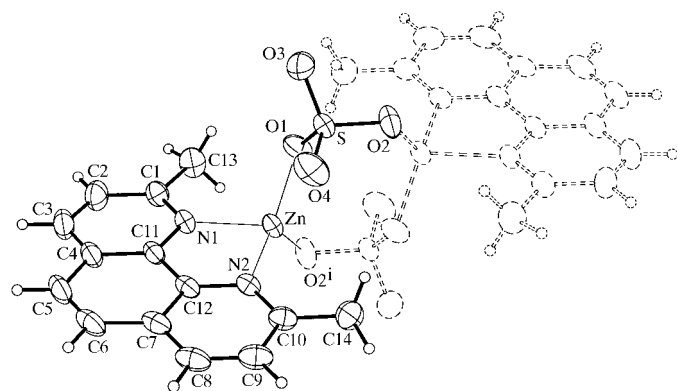

Figure 1

Molecular diagram for (I). Displacement ellipsoids are drawn at the 50% probability level. Light broken lines depict intermolecular hydrogen-bonding interactions; heavy broken lines, intramolecular ones [symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$; (iii) $x, y, 1 + z$].

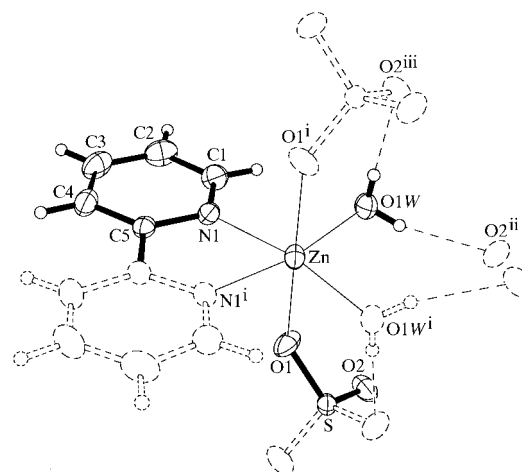
and *catena*-poly[[diaqua(2,2'-bipyridyl-*N,N'*)zinc(II)]- μ -(sulphato-*O:O'*)], (III).

The structure of (I) is made up of monomers (Fig. 1) strongly interlinked by hydrogen bonding. The environment of the cation is octahedral, the bidentate bipy and two aqua molecules occupying the equatorial sites, with a third aqua and one of the sulfate O atoms (the only one involved in direct coordination to the cation) filling the apical sites. There is a strong intramolecular hydrogen bond between one of the coordinated water molecules (O2W) and a second oxygen from the sulfate anion (O4). The rest of the available H atoms take part in important hydrogen-bonding interactions (Table 1) which give rise to a rather complex three-dimensional structure. The O4 atom, in particular, is the acceptor of three interactions, a fact which seems to weaken the S—O4 bond (see below).

In the neocuproine sulfate, (II), the sulfate acts as an O—S—O bridge across two different Zn^{II} nuclei, determining the formation of a dimer (Fig. 2). The cation environment is tetrahedral, the coordination being completed by a bidentate neocuproine. The structure is doubly unique in that it is the first sulfato-bridged zinc(II) dimer reported, and it is the first


Figure 2

Molecular diagram for (II) showing the dimer formed around the symmetry center. Displacement ellipsoids are drawn at the 50% probability level.


Figure 3

Molecular diagram for (III). Note the twofold axis across the coordination polyhedron through the cation. Displacement ellipsoids are drawn at the 50% probability level. Light broken lines depict intermolecular hydrogen-bonding interactions; heavy broken lines, intramolecular ones [symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, 1 - y, \frac{1}{2} + z$; (iii) $x, y, 1 + z$].

Zn^{II} complex with a tetrahedral ZnN₂O₂ environment which includes a bidentate N—Zn—N bite. No hydrogen bonding is present in the structure due to the absence of H-atom donors.

Finally, the bipyridine structure is a polymer made up of ZnN₂O₄ octahedra, with a twofold axis bisecting the coordination polyhedron through the cation and the central point of the bipy ligand. As a result, only half of the group is independent (Fig. 3). The equatorial plane is similarly defined as the one in (I), but the apical sites are provided by a single O atom from the sulfate group. The latter anion, in turn, is also bisected by a second twofold axis thus rendering only two O atoms independent, *i.e.* the one involved in coordination to Zn and a second one which takes part in two important hydrogen bonds; these are an intramolecular one, with one of the two aqua H atoms, H1WA, and an intermolecular one with the remaining hydrogen H1WB.

A systematic analysis of the three structures leads to the conclusion that the S—O bond lengths are quite sensible to the degree of compromise with which the O atoms are involved in any extra interaction, be it coordination or hydrogen bonding. Thus, when coordination is achieved through a mild interaction, *viz* through the occupation of an apical site in a Jahn–Teller distorted octahedron [cases (I) and (III)], the S—O distance hardly departs from average. Instead, when the coordination interaction is strong [case (II)] or the hydrogen bonds in which it takes part are strong and multiple [case of the triple acceptor O4 in (I)], the S—O weakens sensibly with appreciable lengthening of up to 4–5%.

Experimental

The three compounds were obtained by diffusion, following a similar setup: this consisted of two vessels, the first containing an aqueous solution of zinc sulfate [0.050 M in (I) and (II), and 0.025 M in (III)] and the second, a methanolic solution of the corresponding organic

ligand. The link between the two solutions was achieved through a connecting pipe full of water, and after a rather long time (one to two months), some crystals adequate for X-ray diffraction appeared, usually in the connecting media and far from the original solutions. It was not uncommon to have crystals growing in different sections of the setup, which proved to be the same compounds despite displaying quite different habits. The characteristics reported herein are those of the crystals actually measured.

Compound (I)

Crystal data

[Zn(SO₄)(C₁₂H₈N₂)(H₂O)₃]₂·H₂O
 $M_r = 413.70$
 Triclinic, $P\bar{1}$
 $a = 8.641$ (3) Å
 $b = 11.600$ (3) Å
 $c = 8.0460$ (10) Å
 $\alpha = 92.11^\circ$
 $\beta = 103.77$ (3)°
 $\gamma = 92.06^\circ$
 $V = 782.0$ (4) Å³
 $Z = 2$
 $D_x = 1.757$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 7.5$ – 15.0°
 $\mu = 1.749$ mm⁻¹
 $T = 293$ (2) K
 Prismatic, colorless
 $0.35 \times 0.25 \times 0.18$ mm

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (Molecular Structure Corporation, 1988)
 $T_{\min} = 0.63$, $T_{\max} = 0.73$
 4231 measured reflections
 3591 independent reflections
 3355 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 27.47^\circ$
 $h = -8 \rightarrow 11$
 $k = -15 \rightarrow 15$
 $l = -10 \rightarrow 10$
 3 standard reflections every 150 reflections
 intensity decay: <3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.090$
 $S = 1.034$
 3591 reflections
 251 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.496P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.01$
 $\Delta\rho_{\text{max}} = 0.69$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.58$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.106 (4)

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

Zn—O2W	2.076 (2)	Zn—O1W	2.192 (2)
Zn—O3W	2.076 (2)	S—O1	1.461 (2)
Zn—N1	2.132 (2)	S—O2	1.473 (2)
Zn—N2	2.138 (2)	S—O3	1.479 (2)
Zn—O3	2.161 (2)	S—O4	1.504 (2)

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

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WA...O4W ⁱ	0.86 (4)	1.94 (3)	2.783 (3)	167 (3)
O1W—H1WB...O4W	0.76 (3)	2.07 (3)	2.812 (3)	163 (3)
O2W—H2WA...O4	0.80 (4)	1.86 (4)	2.647 (2)	166 (4)
O2W—H2WB...O2 ⁱⁱ	0.83 (4)	1.92 (3)	2.746 (3)	174 (3)
O3W—H3WA...O4 ⁱⁱⁱ	0.83 (3)	1.93 (3)	2.760 (2)	175 (3)
O3W—H3WB...O1 ⁱⁱⁱ	0.87 (4)	1.85 (4)	2.708 (2)	169 (3)
O4W—H4WA...O2 ⁱⁱ	0.78 (4)	2.00 (4)	2.740 (2)	159 (4)
O4W—H4WB...O4 ⁱⁱⁱ	0.80 (4)	1.98 (4)	2.775 (3)	175 (4)

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

Compound (II)

Crystal data

[Zn₂(SO₄)₂(C₁₄H₁₂N₂)₂]
 $M_r = 739.37$
 Triclinic, $P\bar{1}$
 $a = 8.8044$ (15) Å
 $b = 10.4281$ (13) Å
 $c = 8.7719$ (12) Å
 $\alpha = 103.738$ (12)°
 $\beta = 99.385$ (14)°
 $\gamma = 113.357$ (11)°
 $V = 687.70$ (17) Å³
 $Z = 1$
 $D_x = 1.785$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 7.5$ – 15.0°
 $\mu = 1.957$ mm⁻¹
 $T = 293$ (2) K
 Prismatic, colorless
 $0.40 \times 0.28 \times 0.20$ mm

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (Molecular Structure Corporation, 1988)
 $T_{\min} = 0.56$, $T_{\max} = 0.68$
 4198 measured reflections
 3175 independent reflections
 2966 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 27.48^\circ$
 $h = -2 \rightarrow 11$
 $k = -13 \rightarrow 13$
 $l = -11 \rightarrow 11$
 3 standard reflections every 150 reflections
 intensity decay: <3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.096$
 $S = 1.077$
 3175 reflections
 202 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.430P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.01$
 $\Delta\rho_{\text{max}} = 0.85$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.62$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.055 (4)

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

Zn—O2 ⁱ	1.923 (2)	S—O4	1.437 (2)
Zn—O1	1.928 (2)	S—O3	1.439 (2)
Zn—N2	2.035 (2)	S—O2	1.499 (2)
Zn—N1	2.049 (2)	S—O1	1.513 (2)

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

Compound (III)

Crystal data

[Zn(SO₄)(C₁₀H₈N₂)(H₂O)₂]
 $M_r = 353.65$
 Monoclinic, $C2/c$
 $a = 15.421$ (3) Å
 $b = 12.701$ (3) Å
 $c = 6.6940$ (10) Å
 $\beta = 102.13$ (3)°
 $V = 1281.8$ (4) Å³
 $Z = 4$
 $D_x = 1.833$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 7.5$ – 15.0°
 $\mu = 2.106$ mm⁻¹
 $T = 293$ (2) K
 Plate, colorless
 $0.25 \times 0.22 \times 0.12$ mm

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (Molecular Structure Corporation, 1988)
 $T_{\min} = 0.60$, $T_{\max} = 0.78$
 1524 measured reflections
 1473 independent reflections
 1099 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 27.50^\circ$
 $h = 0 \rightarrow 20$
 $k = 0 \rightarrow 16$
 $l = -8 \rightarrow 8$
 3 standard reflections every 150 reflections
 intensity decay: <3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2)]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$(\Delta/\sigma)_{\max} < 0.01$
$wR(F^2) = 0.085$	$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
$S = 1.018$	$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$
1473 reflections	Extinction correction: <i>SHELXL97</i>
102 parameters	(Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0045 (4)

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

Zn—O1W	2.063 (2)	S—O1	1.472 (2)
Zn—N1	2.107 (2)	S—O2 ⁱ	1.478 (2)
Zn—O1	2.226 (2)	S—O2	1.478 (2)
S—O1 ⁱ	1.472 (2)		

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

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WA \cdots O2 ⁱ	0.76 (2)	1.90 (3)	2.658 (3)	177 (3)
O1W—H1WB \cdots O2 ⁱⁱ	0.76 (3)	1.98 (3)	2.714 (3)	165 (3)

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

H atoms attached to carbon were idealized and allowed to ride, except those pertaining to the methyl groups, which were also allowed to rotate around the C—C bond. Those attached to oxygen were found in the difference Fourier map and refined with individual isotropic displacement parameters.

For all 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 structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *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).

This work was partially supported by a CONICET grant (PIP 0470/98). We thank the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1468). Services for accessing these data are described at the back of the journal.

References

- Ali, B., Dance, I. G., Craig, D. C. & Scudder, M. L. (1998). *J. Chem. Soc. Dalton Trans.* pp. 1661–1667.
- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Andreetti, G. D., Cavalca, L. & Musatti, A. (1968). *Acta Cryst.* **B24**, 683–690.
- Burley, S. K., David, P. R., Sweet, R. M., Taylor, A. & Lipscomb, W. N. (1992). *J. Mol. Biol.* **124**, 113–117.
- Dubler, E., Hanggi, G. & Schmalke, H. (1990). *Inorg. Chem.* **29**, 2518–2523.
- Greener, B., Moore, M. H. & Walton, P. H. (1996). *Chem. Commun.* pp. 27–28.
- Hanggi, G., Schmalke, H. & Dubler, E. (1988). *Inorg. Chem.* **27**, 3131–3137.
- Huogh, E., Hansen, L. K., Birknes, B., Jynge, K., Hansen, S., Hardvick, A., Little, C., Dodson, E. & Derewenda, Z. (1989). *Nature*, **338**, 357–359.
- Labadi, I., Pakanyi, L., Kenessey, G. & Liptay, G. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 333–338.
- 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.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1994). *SHELXTL/PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Shorsheneva, Z., Imanakunov, B. I. & Sabirov, V. K. (1994). *Koord. Khim.* **20**, 178–182.
- Songping, D. H., Xiong, R.-G. & Sotero, P. H. (1998). *J. Solid State Chem.* **138**, 361–364.
- Zhang, C., Yu, K., Wu, D. & Zhao, C. (1999). *Acta Cryst.* **C55**, 1815–1817.
- Zhu, Z.-G., Jin, Z.-S., Liu, J.-T., Liu, W.-M. & Ma, D.-G. (1990). *Chin. Sci. Bull. (Engl.)*, **35**, 1521–1525.