Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# (2,2′-Bipyridine-$\kappa^2N,N'$)(1,1-cyclobutanedicarboxylato-$\kappa^2O,O'$)-palladium(II), (1,1-cyclobutanedicarboxylato-$\kappa^2O,O'$)(1,10-phenanthroline-$\kappa^2N,N'$)palladium(II) monohydrate and (1,1-cyclobutanedicarboxylato-$\kappa^2O,O'$)(1,10-phenanthroline-$\kappa^2N,N'$)palladium(II) dihydrate

**Yasunori Muranishi and Nobuo Okabe***

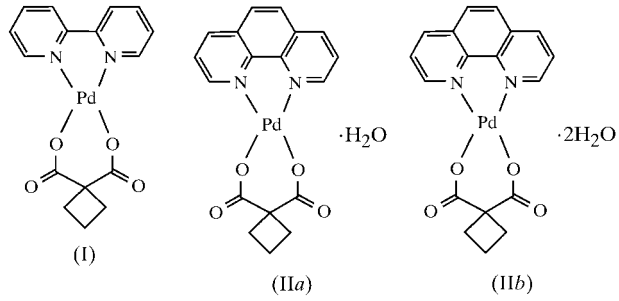
Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashiosaka, Osaka 577-8502, Japan
Correspondence e-mail: okabe@phar.kindai.ac.jp

Received 21 November 2003
Accepted 5 December 2003
Online 10 January 2004

In the three title compounds, $[Pd(C_6H_6O_4)(C_{10}H_8N_2)]$, (I), $[Pd(C_6H_6O_4)(C_{12}H_8N_2)]\cdot H_2O$, (II*a*), and $[Pd(C_6H_6O_4)(C_{12}H_8N_2)]\cdot 2H_2O$, (II*b*), respectively, each $Pd^{II}$ atom has a similar distorted *cis*-planar four-coordination geometry, completed by two O atoms of a bidentate 1,1-cyclobutanedicarboxylate anion and two N atoms of either a 2,2′-bipyridine or a 1,10-phenanthroline ligand.

## Comment

Square-planar $Pt^{II}$ complexes, such as cisplatin [*cis*-diamminedichloroplatinum(II)] or carboplatin [*cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II)], have been used as therapeutic anticancer drugs, with carboplatin, containing the bidentate 1,1-cyclobutanedicarboxylate (cbdca) ligand, displacing fewer side effects than cisplatin (Jakupec *et al.*, 2003). The $Pd^{II}$ analogues of such $Pt^{II}$ complexes have been used as good models for studies of the chemistry of square-planar complexes (Rau & van Eldik, 1996). For example, *cis*-diammine(1,1-cyclobutanedicarboxylato)palladium(II) (Barnham *et al.*, 1994) is isostructural with carboplatin (Beagley *et al.*, 1985; Neidle *et al.*, 1980). Recently, a palladium complex with an aromatic heterocyclic ligand, [Pd(bpy)(cbdca)] (where bpy is 2,2′-bipyridine), has been shown to have better cytotoxic activity than cisplatin against $P_{388}$ lymphocytic leukaemia cells (Mansuri-Torshizi *et al.*, 2001). The aromatic heterocycles can stack with nucleobases and enhance complex formation with DNA, which is the principal target in the chemotherapy of tumours (Shehata, 2001). In this study, we have prepared the $Pd^{II}$ analogues of carboplatin complexes with the aromatic heterocyclic ligands bpy and 1,10-phenanthroline (phen), and determined the structures of [Pd(bpy)(cbdca)], (I), [Pd(phen)(cbdca)]·$H_2O$, (II*a*), and [Pd(phen)(cbdca)]·$2H_2O$, (II*b*). The results are presented here.




The central Pd atom of each complex has the same distorted *cis*-square-planar coordination geometry involving two N atoms of the heterocycle and two O atoms of the cbdca ligand (Figs. 1–3). The bpy plane is mostly perpendicular to the cyclobutane plane. The Pd atom and cbdca ligand form a six-membered chelate ring in a boat conformation, while the aromatic heterocyclic ligand makes a planar five-membered chelate ring. In (II*b*), there are two independent molecules in the asymmetric unit. The molecular structures of (II*a*) and (II*b*) are similar.

The bond lengths and angles in (I), (II*a*) and (II*b*) are very similar (Tables 1, 2 and 4) and may be compared with those reported for $[Pd(NH_3)_2(cbdca)]$ [(III); Barnham *et al.*, 1994] and [Pd(en)(cbdca)] [(IV); en is ethylenediamine; Tercero *et al.*, 2003]. The Pd—N and Pd—O bond lengths in (I), (II*a*) and (II*b*) are in the ranges 1.991 (5)–2.010 (4) and 1.982 (3)–2.005 (4) Å, respectively, which are slightly shorter than those in (III) and (IV) [2.020 (7)–2.030 (2) Å for Pd—N and 2.005 (2)–2.017 (6) Å for Pd—O]. Therefore, the coordination bonds in the title compounds may be somewhat stronger than those in (III) and (IV). The O—Pd—O chelate angles in (I),

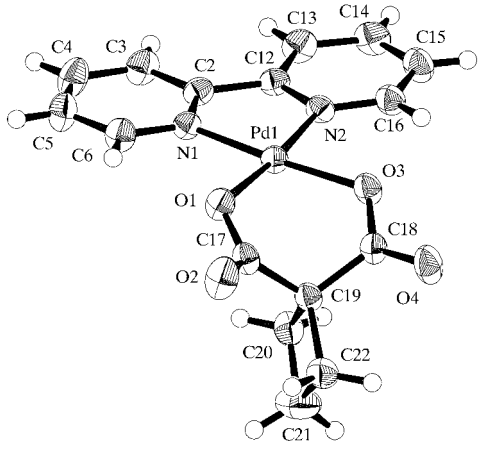



**Figure 1**
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

 DOI: 10.1107/S0108270103028130  

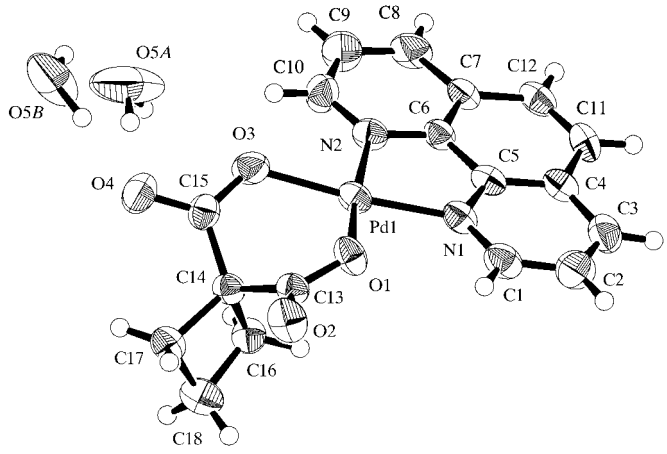



**Figure 2**
The molecular structure of (II*a*), showing the atom-numbering scheme and both sites of the disordered water molecule. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

(II*a*) and (II*b*) are similar to those observed in (III) and (IV) [90.9 and 92.69 (7)°, respectively]. The bpy N—Pd—N chelate angle in (I) and the phen N—Pd—N chelate angles in (II*a*) and (II*b*), are slightly smaller than the value of 84.15 (8)° for en in (IV), and much smaller than the $NH_3$—Pd—$NH_3$ bond angle of 95.0° in (III).

The crystal structure of (I) is stabilized by stacking interactions between bpy ligands related by a centre of symmetry, with a distance between the planes of 3.685 (2) Å. In (II*a*), no stacking interactions between phen ligands are present, and the complexes are connected to each other by hydrogen-bonding networks involving disordered water molecules (Table 3). In (II*b*), there are stacking interactions between phen ligands related by a centre of symmetry, the distances between the planes being 3.379 (6) and 3.360 (7) Å for Pd1···Pd1 and Pd2···Pd2 pairs, respectively. Furthermore, the complex molecules are connected to each other by hydrogen-bonding networks involving the water molecules (Table 5).

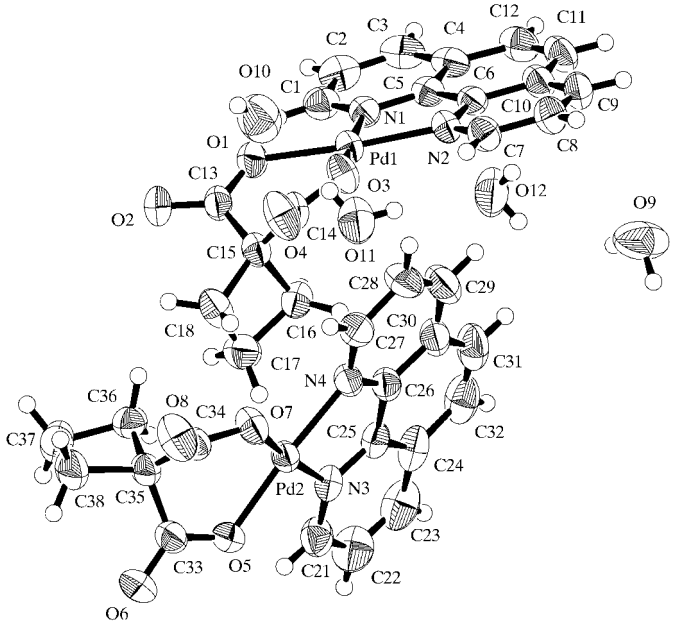



**Figure 3**
The structures of the two independent molecules of (II*b*), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

## Experimental

For the preparation of compound (I), [Pd(bpy)(cbdca)], bpy was reacted with palladium acetate, [$Pd(CH_3COOH)_2$], for 15 min at room temperature (molar ratio 1:1) in dimethylformamide, followed by the addition of an equimolar amount of 1,1-cyclobutanedicarboxylic acid. This mixture was left to stand at room temperature and pale-yellow prism-shaped crystals of (I) appeared after a few days. Compound (II), [Pd(phen)(cbdca)], was synthesized using a method similar to that used for (I), except that phen was used in place of bpy. Crystals of the monohydrate, (II*a*), appeared after a few days. A small quantity of crystals of the dihydrate, (II*b*), appeared in the same crystallizing vessel with (II*a*). The crystals of (II*b*) are rectangular, thin and plate-like, while those of (II*a*) are prisms. The colour of the crystals is pale yellow for both (II*a*) and (II*b*).

### Compound (I)

*Crystal data*

| | |
|---|---|
| [$Pd(C_6H_6O_4)(C_{10}H_8N_2)$] | $Z = 2$ |
| $M_r = 404.71$ | $D_x = 1.857$ Mg m$^{-3}$ |
| Triclinic, $P\overline{1}$ | Mo $K\alpha$ radiation |
| $a = 9.087$ (1) Å | Cell parameters from 25 reflections |
| $b = 9.440$ (1) Å | $\theta = 14.9$–$15.0°$ |
| $c = 9.9820$ (9) Å | $\mu = 1.31$ mm$^{-1}$ |
| $\alpha = 90.458$ (9)° | $T = 296.2$ K |
| $\beta = 113.095$ (9)° | Prism, yellow |
| $\gamma = 111.077$ (9)° | 0.35 × 0.20 × 0.10 mm |
| $V = 723.78$ (15) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Rigaku AFC-5*R* diffractometer | $R_{int} = 0.014$ |
| $\omega/2\theta$ scans | $\theta_{max} = 27.5°$ |
| Absorption correction: $\psi$ scan (North *et al.*, 1968) | $h = -11 \rightarrow 11$ |
| $T_{min} = 0.732$, $T_{max} = 0.878$ | $k = 0 \rightarrow 12$ |
| 3512 measured reflections | $l = -12 \rightarrow 12$ |
| 3315 independent reflections | 3 standard reflections every 150 reflections |
| 3005 reflections with $I > 2\sigma(I)$ | intensity decay: 0.9% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R(F) = 0.022$ | $w = 1/[\sigma^2(F_o^2) + (0.0245P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.057$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.30$ | $\Delta\rho_{max} = 0.40$ e Å$^{-3}$ |
| 3315 reflections | $\Delta\rho_{min} = -0.45$ e Å$^{-3}$ |
| 208 parameters | |

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

| | | | |
|---|---|---|---|
| Pd1—O1 | 2.002 (2) | Pd1—N1 | 1.999 (2) |
| Pd1—O3 | 2.004 (2) | Pd1—N2 | 1.998 (2) |
| | | | |
| O1—Pd1—O3 | 91.68 (7) | O3—Pd1—N1 | 174.37 (9) |
| O1—Pd1—N1 | 93.94 (8) | O3—Pd1—N2 | 93.57 (8) |
| O1—Pd1—N2 | 174.40 (6) | N1—Pd1—N2 | 80.80 (8) |

## Compound (IIa)

*Crystal data*

$[Pd(C_6H_6O_4)(C_{12}H_8N_2)]\cdot H_2O$
$M_r$ = 446.75
Orthorhombic, *Pnn*2
$a$ = 17.219 (2) Å
$b$ = 18.875 (2) Å
$c$ = 5.268 (2) Å
$V$ = 1712.2 (7) Å$^3$
$Z$ = 4
$D_x$ = 1.733 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 14.7–15.0°
$\mu$ = 1.12 mm$^{-1}$
$T$ = 296.2 K
Prism, pale yellow
0.50 × 0.30 × 0.20 mm

*Data collection*

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.736, $T_{max}$ = 0.800
2177 measured reflections
2177 independent reflections
1839 reflections with $I > 2\sigma(I)$
$\theta_{max}$ = 27.5°
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 6$
3 standard reflections
every 150 reflections
intensity decay: 0.8%

*Refinement*

Refinement on $F^2$
$R(F)$ = 0.028
$wR(F^2)$ = 0.079
$S$ = 1.20
2177 reflections
244 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 2.17P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.60 e Å$^{-3}$
Absolute structure: Flack (1983), no Friedel pairs
Flack parameter = 0.17 (6)

**Table 2**
Selected geometric parameters (Å, °) for (II*a*).

| | | | |
|---|---|---|---|
| Pd1—O1 | 2.003 (4) | Pd1—N1 | 1.991 (5) |
| Pd1—O3 | 2.005 (4) | Pd1—N2 | 1.994 (5) |
| O1—Pd1—O3 | 91.3 (2) | O3—Pd1—N1 | 174.7 (2) |
| O1—Pd1—N1 | 93.0 (2) | O3—Pd1—N2 | 93.2 (2) |
| O1—Pd1—N2 | 173.2 (2) | N1—Pd1—N2 | 82.2 (2) |

**Table 3**
Hydrogen-bonding geometry (Å, °) for (II*a*).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O5*A*—H5*AA*···O4 | 1.07 | 2.11 | 3.17 (2) | 177 |
| O5*B*—H5*BA*···O4 | 0.92 | 1.83 | 2.753 (12) | 179 |
| O5*A*—H5*AB*···O5*B*$^{i}$ | 1.06 | 2.18 | 3.24 (4) | 179 |
| O5*B*—H5*BB*···O5*A*$^{ii}$ | 0.99 | 1.99 | 2.99 (3) | 179 |

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

## Compound (IIb)

*Crystal data*

$[Pd(C_6H_6O_4)(C_{12}H_8N_2)]\cdot 2H_2O$
$M_r$ = 464.76
Triclinic, $P\overline{1}$
$a$ = 11.079 (2) Å
$b$ = 11.826 (3) Å
$c$ = 13.678 (4) Å
$\alpha$ = 85.50 (2)°
$\beta$ = 84.55 (2)°
$\gamma$ = 85.87 (2)°
$V$ = 1774.7 (8) Å$^3$
$Z$ = 4
$D_x$ = 1.740 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 14.3–15.0°
$\mu$ = 1.09 mm$^{-1}$
$T$ = 296.2 K
Plate, pale yellow
0.20 × 0.20 × 0.10 mm

*Data collection*

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.777, $T_{max}$ = 0.897
8545 measured reflections
8164 independent reflections
5125 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.033
$\theta_{max}$ = 27.5°
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections
every 150 reflections
intensity decay: 2.1%

*Refinement*

Refinement on $F^2$
$R(F)$ = 0.040
$wR(F^2)$ = 0.118
$S$ = 0.99
8164 reflections
487 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.44 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.79 e Å$^{-3}$

**Table 4**
Selected geometric parameters (Å, °) for (II*b*).

| | | | |
|---|---|---|---|
| Pd1—O1 | 2.001 (3) | Pd2—O5 | 1.997 (4) |
| Pd1—O3 | 1.982 (3) | Pd2—O7 | 1.995 (3) |
| Pd1—N1 | 2.002 (4) | Pd2—N3 | 2.001 (4) |
| Pd1—N2 | 2.010 (4) | Pd2—N4 | 2.007 (4) |
| O1—Pd1—O3 | 92.8 (1) | O5—Pd2—O7 | 92.6 (1) |
| O1—Pd1—N1 | 93.3 (1) | O5—Pd2—N3 | 92.7 (2) |
| O1—Pd1—N2 | 174.7 (1) | O5—Pd2—N4 | 174.4 (1) |
| O3—Pd1—N1 | 172.7 (2) | O7—Pd2—N3 | 173.5 (2) |
| O3—Pd1—N2 | 91.6 (1) | O7—Pd2—N4 | 92.7 (1) |
| N1—Pd1—N2 | 82.1 (1) | N3—Pd2—N4 | 82.0 (2) |

**Table 5**
Hydrogen-bonding geometry (Å, °) for (II*b*).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O9—H9*A*···O6$^{i}$ | 0.94 | 1.82 | 2.756 (6) | 179 |
| O9—H9*B*···O8$^{ii}$ | 0.92 | 1.91 | 2.822 (6) | 177 |
| O10—H10*A*···O2$^{iii}$ | 0.82 | 2.26 | 3.056 (6) | 165 |
| O10—H10*B*···O9$^{iv}$ | 0.87 | 1.99 | 2.853 (8) | 175 |
| O11—H11*A*···O10 | 0.81 | 2.07 | 2.881 (7) | 176 |
| O11—H11*B*···O12 | 0.80 | 2.02 | 2.822 (6) | 175 |
| O12—H12*A*···O2$^{v}$ | 0.81 | 2.08 | 2.850 (5) | 159 |
| O12—H12*B*···O4$^{iv}$ | 0.80 | 2.08 | 2.848 (5) | 159 |

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

For (I), all H atoms were located in difference Fourier maps and were then regenerated at ideal positions by riding models using HFIX instructions (*SHELXL*97; Sheldrick, 1997). In (II*a*), there is positional disorder of the water molecule over two sites, O5*A* and O5*B*; the site-occupancy factors were assigned as 43 and 57%, respectively. For (II*a*) and (II*b*), all H atoms were located in difference Fourier maps and were then, except for those of the water molecules, regenerated at ideal positions by riding models using HFIX instructions. The H atoms of the water molecules were fixed at the positions located in difference Fourier maps.

For all three compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000). For compound (I), program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999). For compounds (II*a*) and (II*b*), program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997). For all three compounds,

program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1156). Services for accessing these data are described at the back of the journal.

## References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Barnham, K. J., Djuran, M. I., Frey, U., Mazid, M. A. & Sadler, P. J. (1994). *J. Chem. Soc. Chem. Commun.* pp. 65–66.

Beagley, B., Cruickshank, D. W. J., McAuliffe, C. A., Pritchard, R. G., Zaki, A. M., Beddoes, R. L., Cernik, R. J. & Mills, O. S. (1985). *J. Mol. Struct.* **130**, 97–102.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Jakupec, M. A., Galanski, M. & Keooler, B. K. (2003). *Rev. Physiol. Biochem. Pharmacol.* **146**, 1–53.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mansuri-Torshizi, H., Ghadimy, S. & Akbarzadeh, N. (2001). *Chem. Pharm. Bull.* **49**, 1517–1520.

Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. Version 5.32. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (2000). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Neidle, S., Ismail, I. M. & Sadler, P. J. (1980). *J. Inorg. Biochem.* **13**, 205–212.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Rau, T. & van Eldik, R. (1996). *Metal Ions in Biological Systems*, Vol. 32, edited by A. Sigel & M. Sigel, pp. 339–378. New York: Marcel Dekker.

Shehata, M. (2001). *Transition Met. Chem.* **26**, 198–204.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Tercero, J. M., Matilla, A., Sanjuan, M. A., Moreno, C. F., Martin, J. D. & Walmsley, J. A. (2003). *Inorg. Chem. Acta*, **342**, 77–87.